



# THE HYDROGENATION OF OILS

CATALYZERS AND CATALYSIS

AND THE

GENERATION OF HYDROGEN AND OXYGEN

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## PREFACE TO THE SECOND EDITION

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SINCE the first edition of this volume was published in 1914, the strides made in the oil-hardening industry have surpassed all expectations. The advances effected by inventors in simplifying old methods and creating new ones and the wider adaptation of the process in the hands of skillful factory operators have led to many changes and betterments. The present edition endeavors to bring the developments in this field down to date, and to offer suggestions of future possibilities. Unexpected uses for hydrogenated oils have been and continue to be discovered, hence the market for these fats is constantly broadening. After finding a secure place for the production of edible fats in this country, the hydrogenation process has also been taken up more seriously by the soap-maker, and with the scarcity of natural tallow due to war conditions, has enabled the soap manufacturer to produce an artificial tallow from relatively cheap oils. During the past two years this has been accomplished on a large scale.

Much of historical and general interest will be found in the records of patent litigation in this country, appearing in the appendix. The details of the beginning of oil hardening in the United States, which hitherto seemingly have been surrounded by a veil of mystery, are now accessible to the reader.

Owing to certain difficulties of classification, an unusually complete index is appended.

C. E.

92 GREENWOOD AVENUE,  
MONTCLAIR, N. J.  
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## PREFACE TO THE FIRST EDITION

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THE course of development of the oil industry is marked by the milestones of discovery, embracing glycerine recovery, hydrolytic saponification, the Twitchell process, the distillation of fatty acids, the Wesson process of oil deodorization, the pioneer work of Mège-Mouries and the resulting margarine industry, the intimate incorporation of oil and steam by sudden chilling to form lard compound, the desulfurization of petroleum oils by copper oxide; and to the foregoing should be added a comparatively recent discovery, the technical hydrogenation of oils, which is destined to take a very prominent place in the oil industry. The extensive use of the hydrogenation process is beyond doubt, it must in fact be regarded as the most important advance in the technology of oils during recent years. The probable effect on the oil and allied industries and on the oil and oil seed markets is difficult to forecast, as the full possibilities of the process cannot yet be determined.

The whole structure of hydrogenation resides in the catalytic action of practically only a limited number of metals and their compounds, which awaken the usually passive element hydrogen from its dormant condition and thus enable its combination with unsaturated bodies. Often the term catalysis is said to be an overworked expression under cover of which chemists may find refuge when pressed for an explanation of obscure phenomena. But whether or not the term is overworked it is indeed certain that with rational treatment catalyzers are the hardest workers in the domain of chemistry and may effect the transformation of a prodigious amount of raw material without detriment to themselves unless perchance their labors are checked by the accidental presence of certain unfriendly bodies or catalyzer "poisons" as these are termed.

In 1823 Doberiner found that hydrogen would ignite, when, in the presence of air, it was exposed to finely-divided platinum, and this manifestation of catalytic activity by platinum and also palladium was studied during the middle of the last century by Liebig, Debus and others. In 1888 Mond made use of reduced nickel on a porous carrier, curiously enough not to add hydrogen but to eliminate it, thus providing a method of preparing hydrogen gas. Ten years or

so later, Sabatier and Senderens reversed this procedure and made such nickel carry hydrogen to unsaturated organic compounds of a character which could be vaporized readily. Then in 1903 came Normann who disclosed the application of nickel catalyzer to the hydrogenation of fixed or fatty oils or the production of stearin from olein. But it was years afterwards before the idiosyncrasies of catalytic nickel were fully understood and the technical difficulties of hydrogenation were surmounted so as to afford eminently practical results.

To-day this branch of the oil industry is growing by leaps and bounds and its advent into the field has brought a flood of congratulations, protests and criticisms, market disturbances, and great activity among chemists to improve the catalytic materials and processes of treatment involved.

The present book it is hoped will be of assistance to the practical worker as well as to the student of oils and fats. It has been the outgrowth of a number of years of observation and experience involving the collection of a considerable amount of data from many sources. An attempt was made by the author to present the matter in brief form before the Society of Chemical Industry in 1912 and the present volume is based on the general plan or arrangement of material adopted in that paper.

Heretofore, the literature on hydrogenation has been scattered through many periodicals and no effort has been made to collect this material and arrange it in book form, although the treatises of Hefter and Ubbelohde and Goldschmidt include a few pages on the conversion of soft fats by various methods to stearic acid or stearin; but such reviews have been too brief to afford the practical operator sufficient working material.

A considerable mass of data including practically all that has been advanced on the subject of hydrogenation of fatty oils has been collected and arranged in this volume. The observations and opinions of many minds have been brought together. Some of these views obviously are sound, others are open to grave doubt and still others are of a contradictory or polemical nature. Whether or not in the treatment of this material to carry through a vein of critical comment was a problem which confronted the author and the conclusion was reached that at this stage of a young art, it would be inadvisable in general to do more than array the multitude of processes, formulæ, proposals and opinions, leaving to the reader the selection of that which should prove of greatest utility.

A few years hence when oil hydrogenation will have found its measure and the more important points concerning it have reached

A definite settlement, the allotment of space to a number of the discussions appearing on the following pages would hardly be warranted, but at the present time when many are desirous of having at hand a treatise which comprises all or nearly all the published work to date, containing though it does a considerable divergency of opinion, there appears ample justification for the inclusion of material which later may be considered superfluous.

Frequent reference has been made to the material scattered through the literature and acknowledgment is rendered to these sources of information, especially to the Journal of the Society of Chemical Industry and the Seifenseider Zeitung.

C. E.

MONTCLAIR, N. J.

June 15, 1914.



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# THE HYDROGENATION OF OILS

## CHAPTER I

### METHODS OF HYDROGENATION \*

For years the dream of the oil chemist was to find a solution to the problem of converting oleic acid into stearic acid, or olein into stearin, simply by the addition of hydrogen, so as to make valuable hard fats from relatively cheap raw material. Superficially the problem looked simple. Oleic acid is the next door neighbor of stearic acid, apparently differing only in having a little less hydrogen than stearic acid has in its constitution. Only a trifling amount of hydrogen, less than one per cent, is required to transform oleic into stearic acid.

But the problem was far from simple as oleic acid stubbornly resisted the invasion of hydrogen into its structure to any material extent under the earlier methods of hydrogen addition, and not until recent years, with the discovery of effective hydrogen carriers or catalyzers, has it become possible to bring about this conversion economically with large yields so as to warrant commercial exploitation in an extensive way.

Now the problem is solved, and in different parts of the globe dozens of plants turning out daily enormous quantities of "hardened oil" prepared by the treatment of vegetable or other oil with hydrogen have been established.\* So eagerly has the oil handling world lent itself to the idea that already the stearin market has lost its firmness and much speculation is rampant as to the nature of price readjustments which perhaps are on the way. Unquestionably hydrogenated or hardened oil has taken its place in the oil market as a staple product.

### A REVIEW OF THE ART.†‡

Many attempts to hydrogenate oleic acid have been made. Reviewing this subject in 1897 § **Lewkowitsch** refers to the ease with

\* A list of over twenty firms in different parts of the world having plants for hardening oils is found in *Seifensieder Zeitung*, 1914, 349.

† See Ellis, *J. S. C. I.*, 1912, 1155; *J. Ind. Eng. Chem.*, 1913, 95; *The American Perfumer*, 1913.

‡ The production of stearic acid and other acids or products of high melting point from oleic acid is discussed by Hefter, *Technologie der Fette und Öle*, Vol. III, 765 and 994; also by Ubbelohde und Goldschmidt, *Handbuch der Chemie und Technologie der Öle und Fette*, Vol. III, 152.

§ *J. S. C. I.*, 389 (1897).



which the lower members of the oleic series are converted into saturated acids and states that "oleic acid itself resists all attempts at hydrogenization," further remarking that he had "carried out a large number of experiments in this direction under most varied conditions, but hitherto all of these gave negative results."

Prior to this, however, **Goldschmidt**, in 1875,\* had reduced oleic acid by means of hydriodic acid and amorphous phosphorus at 200° to 210° C. This presumably led to the attempted commercial development of a process by **de Wilde and Reychler**† involving heating oleic acid to 280° C. with 1 per cent of iodine, adding and melting therein a certain quantity of tallow soap, and then boiling with acidulated water. The product was then distilled and the iodine, in part, recovered from the pitch. The yield of stearic acid or saturated fat is stated to be approximately 70 per cent of the theoretical. Only about two-thirds of the iodine could be recovered so the process apparently did not find technical use.‡ Should the much lauded method of treating kelp, primarily for obtaining potash salts, come into use, a cheap supply of iodine would be available which might then make the Wilde and Reychler process of some technical interest.

Chlorine in lieu of iodine has been tried, but great difficulty has been experienced in securing an autoclave of resistant material. **Imbert**§ recommends using quantities of chlorine and alkali exactly calculated on the iodine number of the fatty acid and operating at a temperature of 120° to 150° C. and a pressure of about five atmospheres for a period of six hours.

**Zurrer**|| chlorinates the fatty acid and then heats with water in the presence of a finely-divided metal, as zinc or iron. **Lewkowitsch** alleges that the treatment of monochlor-stearic acid in this manner causes a reversion to oleic acid.

**Tissier**, in 1897,¶ lays claim to a process for the reduction of oleic acid by nascent hydrogen. Powdered metallic zinc is placed in an autoclave, water and the fatty material containing olein being introduced, and treated under pressure.

Under the circumstances the glyceride is hydrolyzed to fatty acid and glycerine, and according to **Tissier** nascent hydrogen is evolved by

\* Sitz. b. d. Wiener Akad. d. Wiss., 72, 366.

† Bull. Soc. Chim. [3], 1, 295 (1889).

‡ Chem. Ztg., 1889, 595.

§ U. S. Patent No. 901,905, October 20, 1908; see also Bull. Soc. Chim., 1899, 695, 707.

|| German Patent No. 62,407, August 8, 1891.

¶ French Patent No. 263,158, January 16, 1897.

virtue of the finely-divided metal and reduces the oleic to stearic acid. **Freundlich** and **Rosauer** \* claim the **Tissier** process to be inoperative.

The conversion of oleic acid into palmitic and acetic acids by means of caustic potash in accordance with the **Varentrapp** reaction † has not proved to be of much commercial significance, although it appears that certain firms have been making use of the process in a limited way.

The **Schmidt** zinc chloride process‡ involves heating oleic acid and zinc chloride at exactly 185° C. while interaction is taking place. "Deviation from this point leads to an increase of liquid substance. Unfortunately the solid candle material must be distilled and the considerable proportion of  $\beta$ -hydroxy-stearic acid (melting point 82° C.) in the crude product is seriously diminished by the partial conversion of this acid into oleic and iso-oleic acids. Thus, from a candle-maker's point of view, a substance of high melting point is rendered practically valueless. **Schmidt's** process was tried on the large scale in an Austrian candle works. The quantity of liquid *unsaponifiable* substance obtained was, however, so large that commercial success was out of the question."

Many processes based on the well-known action of sulfuric acid on oleic acid have been proposed. Hydroxy-stearic acid is obtained by steaming the product. It would lead us too far from the present subject to enter into any further discussion of these reactions.

#### PROCESSES INVOLVING APPLICATION OF ELECTRICITY

In 1886 **Weineck** § called attention to the possibility of electrolytic addition of hydrogen to oleic acid. **Kuess** || later attempted to apply the electric current in the steam distillation of fatty acids.

In patents taken out by **Magnier**, **Bagnier** and **Tissier**,¶ the fatty material is acidified with sulfuric acid, whereupon the acidified mass is mixed with 5 to 6 times its weight of water and then under a pressure of 5 atmospheres is subjected to the action of an electric current, which generates hydrogen in a nascent state.

An interesting method of converting oleic into stearic acid is that comprised in the **Hemptinne** electric discharge process. The method

\* Chem. Ztg., 1900, 566.

† J. S. C. I., 98 (1883), 200 (1884).

‡ Lewkowitsch, "Oils, Fats and Waxes," p. 664.

§ Osterr. Privil., 10, 400 (July 19, 1886).

¶ Chem. Ztg., 1896, 618.

|| British Patent 3363, 1900; German Patent 126,446, October 3, 1899, and additional German Patent 132,223.

is carried out by interposing a thin layer of the oil in the path of an electric discharge, while bringing hydrogen into contact with the oil.\*

Fig. 1 shows the arrangement of apparatus for this purpose. The conversion is effected in a chamber having an inlet pipe *H*, furnishing hydrogen under constant pressure. Oleic acid is supplied by a pipe *O* to a sprinkling device which discharges the acid onto a system of parallel plates consisting of the glass plates *G* and alternately the metal plates *M*, *N*. The metal plates *M* are connected to one pole, the others, *N*, being connected with the other pole of a source of electricity.

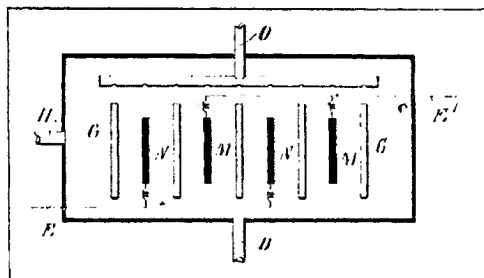


FIG. 1.

As the oil passes over the plates the electrical discharge causes conversion of some oleic acid into stearic acid, and analogous compounds having melting points in the neighborhood of  $69^{\circ}\text{C}$ .

Henmptinne prefers to work at pressures less than atmospheric. The yield is lower at atmospheric pressure. By treatment in this manner it is not difficult to secure a yield of 20 per cent of stearic acid. Repeated treatment permits even up to about 40 per cent yield. Here, as so often elsewhere, the effect of mass action becomes manifest and as the content of stearic acid increases the speed of reaction greatly decreases. Much better results are obtained by saturating to the extent of about 20 per cent, removing the stearic acid by pressing, when the oil of reduced stearic acid content is again subjected to the electric discharge, and a further 20 per cent yield obtained. The oleic residue contains liquid condensation products amounting to about 40 per cent of the total weight. It is stated that the presence of these bodies does not impair the market value of what some one has termed "electrocuted" oleic acid.

\* U. S. Patent 797,112, August 15, 1905.

**Petersen** \* also endeavored to reduce oleic acid to stearic acid by allowing an electric current to act between nickel electrodes on an alcoholic oleic acid solution, slightly acidulated with sulfuric acid or preferably with hydrochloric acid. But the yield of stearic acid was small, even under the most favorable conditions, and did not exceed 15 to 20 per cent.

Petersen also endeavored to reduce sodium oleate in aqueous or alcoholic solution to the stearate. No satisfactory results were obtained.

**C. F. Bohringer and Sohne** † obtained by the same method much better results when using as cathodes, metallic electrodes, which were covered with a spongy layer of the same metal. They recommend as cathodes platinized platinum, and also palladium electrodes covered with a spongy layer of palladium-black. Nickel electrodes are not as effective.

•  
**Bruno Waser** ‡ states that oleic acid or olein should be sulfonated and freed from free sulfuric acid before adding hydrogen electrically (cathodic reduction). As an example, one equivalent of oleic acid is mixed with two or three equivalents of 95 per cent sulfuric acid, the temperature not being permitted to advance more than 5 degrees. The mixture is allowed to stand 24 hours, is then washed with ice cold water and dissolved in boiling water. This solution serves as catholyte, a 30 per cent sulfuric solution being the anode liquid. A diaphragm separates lead electrodes. The temperature is maintained at 90° to 100° C. with a current density of 25 to 100 amperes per square decimeter, giving 60 to 70 per cent conversion to stearic acid.

#### HYDROGENATION BY CATALYTIC ACTION

**Kolbe** § in 1871 states that **Saytzeff** reduced nitrobenzol to aniline by passing the vapors of the former, mingled with hydrogen, over palladium-black.

About twenty-five years later **Sabatier and Senderens** began their classic study of nickel and other metallic catalyzers.

The work of Sabatier and Senderens || laid the foundation for the

\* Z. Elektrochemie, 1905, 549.

† German Patents 187,788, 189,332, 1906

‡ German Patent 247,454, March 24, 1911, and Seifen. Ztg., 1912, 661.

§ J. prakt. Chem. [2], 4, 418 (1871).

|| Sabatier and Senderens published the results of their earlier work in Comp. rend., 132, 210, 566 and 1254. A very complete description of their investigations appears in Ann. de Chim. et de Phys., 1905 (8), 4, 319-488. See also Mailhe Chem. Ztg., 1907 (31), 1083, 1096, 1117, 1146 and 1158; Chem. Ztg., 1908 (32), 229 and

present processes of hydrogenation of oils. These distinguished chemists first recognized the effectiveness of nickel and certain other metals as carriers of hydrogen and they elaborated a series of brilliant experiments extending over a number of years, which demonstrated that unsaturated compounds, that is, bodies lacking in hydrogen, could be saturated or given the full quota of hydrogen by contact with this gas in the presence of a catalyzer or carrier, such as finely-divided nickel. By their painstaking labors the reaction was shown to be one of general application.

Fig. 2 shows the apparatus used by these investigators in the hydrogenation of bodies capable of vaporization. In this apparatus, 1 is

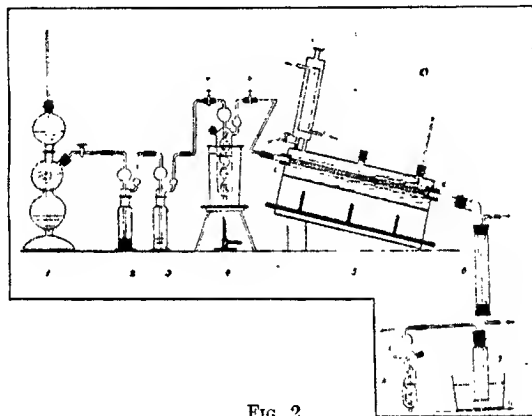


FIG. 2.

a hydrogen generator; 2 and 3 are wash bottles; 4 is a vaporizer containing the substance to be converted into a vapor; 5 is a hydrogen chamber containing nickel catalyzer and heated by an oil bath; and 6 is a condenser.

While a good deal of work has been done on the hydrogenation of fatty oils, the literature on the subject is not very profuse and only through the patents which have been issued can we gather from any

244; Willstätter and Mayer, Ber., 1908 (41), 2199; Paal and Amberger, Ber., 1905 (38), 1406 and 2414; Paal and Gerum, Ber., 1907 (40), 2209; 1908 (41), 813 and 2273; 1909 (42), 1553; Paal and Hartmann, Ber., 1909 (42), 2239; Paal and Roth, Ber., 1908 (41), 2282; 1909 (42), 1541; Ipatiew, Ber., 1902 (35), 1047; 1904 (37), 2961; Chem. Centralbl., 1906, II, 86; Ber., 1907 (40), 1270 and 1286; 1908 (41), 991; 1909 (42), 2089, 2092 and 2100; Ipatiew, Jakowlew and Rakitin, Ber., 1908 (41), 996; Ipatiew and Philipow, Ber., 1908 (41), 1001; Padoa and Carughi, Chem. Centralbl., 1906, II, 1011.

published records much that is enlightening as to some of the technical developments in this industry. The patents concerned with the matter have, moreover, been subjected to a great deal of scrutiny because of the alleged basic character of certain of them. For these reasons the remainder of this chapter pertains very largely to processes which have been covered by patents \* in this country or abroad.†

A German Patent 139,457, of July 26, 1901, to **J. B. Senderens**, is probably the first patent record having to do with the reduction of organic bodies by hydrogen in the presence of nickel catalyzers. This patent is for the production of aniline from nitrobenzol and involves passing the latter body in the form of a vapor over heated nickel, copper, cobalt, iron or palladium in the presence of hydrogen. The hydrogen may be in the pure state or in the form of water-gas.

The first disclosure of the possibility of hydrogenation of oils in a liquid state apparently comes from **Leprince and Siveke**.‡ In England a corresponding patent 1515, of 1903, was issued to **Normann** § and the latter patent has become widely known because of its alleged fundamental character.¶

\* Sachs (*Zeitsch. f. angew. Chem.*, 1913, No. 94, 784) reports 183 patents on oil hardening of which there are 33 German; 22 French; 51 English; 33 United States; 9 Belgium; and 35 in other countries.

† The illustrations immediately following are largely derived from the drawings of patent records or have been prepared from written descriptions. In some cases all details deemed unnecessary in the portrayal of the essential features of these processes have been omitted. The original records should, of course, be consulted for details. — *Author*.

‡ German Patent 141,029, August 14, 1902, *Herforder Maschinenfett und Oelfabrik*.

§ This English patent is owned by a large soap manufacturing house in England and has been passed on unfavorably by the courts. See Appendix.

¶ The *Seifensieder Zeitung* (1913), 1272, states that German Patent 141,029 (Leprince and Siveke) is controlling in that country so far as the use of metallic catalyzers for oil hardening is concerned, because this patent makes the first disclosure of the hydrogenation of bodies in the liquid state by simple addition of a catalyzer and introduction of hydrogen. According to the same journal (1913), 1195, the Bremen-Besigheimer Ölfabriken in Bremen has a large plant for the hydrogenation of fats and oils which at one time was not in use because of patent disputes between this concern and the Germania Company. The Bremen Company has made arrangements with the patent owners and is now operating the Bremen plant. (*Seifen. Ztg.* (1913), 1273.)

Leprince and Siveke (German Patent 141,029 was assigned on July 22, 1910, to Joseph Crosfield & Sons, Ltd., of England and was again assigned on August 9, 1911, to Naamlooze Venootschaap Anton Jurgen's Fabriken, Oss in Holland. The latter concern on the 10th of July, 1911 founded the Oelwerke Germania, G. M. b. H.,

at Emmerich, on the Rhine. The plant is reported to have been put into operation in the Spring of 1912 — almost ten years after the application for German patent 141,029.

The contentions of Professor Erdmann (*Seifen. Ztg.* (1914), 32) present certain points of interest. Referring to German Patent 141,029 which was applied for in 1902 and granted in 1903, Erdmann states that eight years later — without being used regularly on a large scale in Germany — the rights were sold in England to Crosfield & Sons. The requirements for the successful hardening of oils by the use of metallic nickel as a catalyst are regarded as having been here given for the first time.

The German patent application B. 62,366, IV, 12°, of Bedford, Erdmann and Williams for hydrogenating oils with the aid of metallic oxides, was entered on March 16, 1911, together with the English priority of Dec. 20, 1910, a time therefore when the Germania Werke did not exist. In addition, it is stated, Bedford and his colleagues immediately started in to actually materialize their original discoveries and ideas on a large scale; their experimental plant had been working for a considerable period and in Germany at that time oils had not been hardened on a manufacturing scale.

It is not true, Erdmann states, that the process of German patent 141,029 was the first solution of the problem of the direct addition of hydrogen to unsaturated fatty bodies. It does not cover the direct addition of hydrogen — a process for the direct addition of free hydrogen by means of a catalyst involves a contradiction of terms — but aims at the indirect addition to an unsaturated fatty substance by means of a catalytic hydrogen carrier in just the same way as this had already been accomplished previously by Karl Peters (*Monatshefte f. Chemie*, 1886 [7], 552), and Reformatsky (*J. prakt. Chemie N. S.*, 1890 [41], 437) in the hydrogenation of oleic acid to stearic acid by the use of iodine as the hydrogen carrier.

At the time of the application for German patent 141,029 — that is, in 1902 — Erdmann observes that the transformation of unsaturated compounds contained in liquids to saturated compounds by means of the introduction of free hydrogen into the liquid with the aid of a catalyst was not entirely unknown. For example, in 1873, Saytzeff (in Kolbe's laboratory) obtained aminophenol and methylamin by the introduction of free hydrogen into a solution of nitrophenol or nitromethane in the presence of finely-divided palladium. (See *J. prakt. Chemie. N. S.* [6], 128.) In practically the same way, oleic acid could be changed to stearic acid as Pokin later showed (*Chem. Centralbl.* (1907), II, 1324). Hence Erdmann claims it is not true that the existence of the discovery represented by German patent 141,029 can be looked upon as the first time that a means was found to saturate unsaturated substances in the liquid state by means of free hydrogen.

In case any discovery can be found set forth in Patent 141,029 — which according to the statements of the English courts is at least very questionable — the new idea, Erdmann contends, can only be that the two steps:

- (a) Hydrogenation of liquid *organic* substances by the introduction of free hydrogen in the presence of a finely-divided metallic catalyst, and
- (b) Hydrogenation of unsaturated *fatty* substances in the presence of a non-metallic or not finely-divided metallic catalyst,

which steps were known separately, are combined with one another in this way, that fatty substances are hydrogenated by the introduction of free hydrogen in the presence of a finely-divided, metallic catalyst, particularly nickel which was already known to be a hydrogen carrier. Metals, also, — for example zinc — had been pro-

**Normann** states that he may carry out the hydrogenation of oils by treatment either in the form of vapors or as liquids. In the former case the fatty acid vapors together with hydrogen may be caused to pass over catalytic material carried by a pumice stone support. This may be represented by Fig. 3 in which *A* is a bed containing granular pumice coated with a metal catalyzer. *O* is an inlet for oil vapors and *H* is an inlet for hydrogen. The mixture passes through the tube *A* and the converted material is withdrawn at *B*. Normann notes, however, that it is sufficient to expose the fat or fatty acid in a liquid

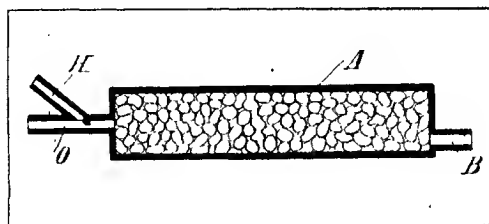


FIG. 3.

condition to the action of hydrogen and the catalytic substance. He states that, for instance, if fine nickel powder obtained by the reduction of nickel oxide in a current of hydrogen is added to oleic acid, the latter heated over an oil bath and a strong current of hydrogen caused to pass through it for a considerable time, the oleic acid may be completely converted into stearic acid.

Fig. 4 shows very simple apparatus, such as might have been used by Normann to this end. *A* is a vessel containing oil *O* in which fine particles of nickel are suspended while a strong current of hydrogen from the pipe *H* affords the hydrogen requisite for reduction of the oil. By this means Normann treated the fatty acid of tallow, having an

posed for the hydrogenation of oleic acid before 1903 (compare Tissier, *Chem. Ztg.*, 1899 [23], 822).

Normann (*Seifen. Ztg.* (1913), 1381) regards the employment of metal oxides or organic salts as catalyzers to fall within the scope of the Leprince and Siveke (Normann) German patent 141,029, because of the reduction occurring when these metallic compounds are exposed to hydrogen in the hardening process. Meigen and Bartels (*J. prakt. Chem.* 1914, 290) support Normann's contention. The assertions of Erdmann regarding the existence of nickel suboxide when hardening oils with nickel oxide catalyzers are challenged by the Ölwerke Germania (*Seifen. Ztg.* 1914, 209) and it is claimed that metallic nickel forms under the conditions to which the oxide is subjected. In this connection, a brief review of Ipatieff's work is given.



iodine number of 35 and melting at about 46, thereby converting it into a body of improved color having an iodine number of about 10, and a melting point of about 58. Normann also states that commercial gas mixtures, such as water-gas, may be used in lieu of pure hydrogen.

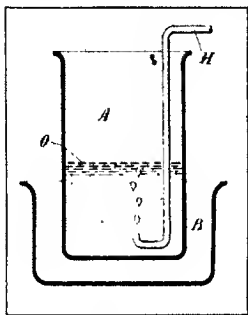


FIG. 4.

The disclosures of the Normann patent are, however, rather meagre and can hardly be considered to comprehensively traverse the difficulties encountered in the practical hydrogenation of oils in a liquid state.

Day has brought out a process\* in which he treats, not fatty oils, but hydrocarbon oils, with hydrogen in the presence of what he terms a porous absorptive substance mentioning palladium black, platinum sponge, zinc dust, fuller's earth and other

clays. Fig. 5 shows one method proposed by Day to this end.

The upper chamber *A* is filled with hydrocarbon oil, and porous absorptive material, such as palladium black, is introduced into the inter-

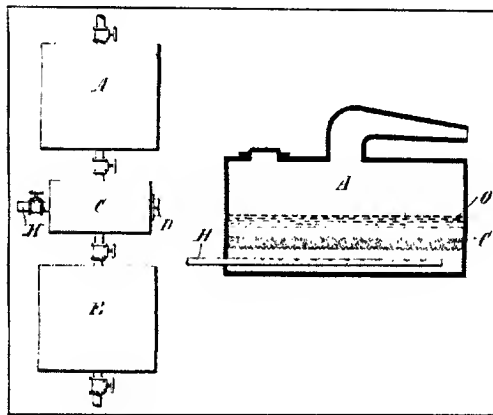


FIG. 5.

FIG. 6.

mediate chamber *C* by way of the plugged orifice *D*. Any air present in *C* may be expelled by flushing out with hydrogen or an indifferent gas. Hydrogen is then admitted by the pipe *H* until the porous

\* U. S. Patent 826,089, July 17, 1906.

material has absorbed its full quota. The hydrogen gas may be admitted under a pressure of 100 pounds or more to the square inch. When the porous material in *C* has become properly charged with hydrogen, the oil is allowed to run from the chamber *A* through the chamber *C* into the collecting chamber *E*, hydrogen being introduced as required by the pipe *H*.

In the place of hydrogen, Day states that ethylene or other hydrogen-carrying gas or vapor may be employed. By this treatment the disagreeable odor of hydrocarbon oil is in great part removed and the burning qualities of the oil improved. When palladium black is used it is recommended that a proportion of one-half ounce to the gallon of oil be taken.

Fig. 6 shows a modification of Day's process. *A* is an oil still, in the lower part of which the perforated pipe *H* serves for the admission of hydrogen. Palladium black or other porous absorptive material forms a layer *C*, on a screen above the hydrogen inlet. *O* shows the charge of oil. In operating this apparatus the layer of material *C* is first charged with hydrogen and then oil run into the still. Distillation is carried out while hydrogen gas is being forced through the absorptive material and oil.\*

\* The removal of sulfur from petroleum is effected according to Schiller (U. S. Patent 580,652, April 13, 1897), by generating hydrogen in a nascent condition in the oil during the distillation of the latter. It is claimed that sulfur is thus eliminated as hydrogen sulfide. Zinc dust and an alkaline hydrate, such as dry powdered caustic soda, are employed to generate hydrogen. These are added to the oil undergoing distillation. Huston (U. S. Patent 486,406, Nov. 15, 1892) proposes to remove sulfur by heating the vapors of a sulfur-containing petroleum oil admixed with steam to a temperature of 900° F. at which temperature it is said that the hydrogen of the water vapor unites with the sulfur, forming hydrogen sulfide. Hawes (U. S. Patent 444,833, Jan. 20, 1891) avails of the same reaction and brings a mixture of vapor of hydrocarbon and water into contact with gravel contained in a chamber which is heated to a temperature of 400° to 600° F. Dubbs (U. S. Patent 470,911, March 15, 1892) forces a gas rich in hydrogen through oil in a still to remove sulfur as hydrogen sulfide. Stevens (U. S. Patent 414,601, Nov. 5, 1889) claims steam reacts with the sulfur present in petroleum oils to form sulfurous acid, while the hydrogen thus liberated combines with the carbon of the oil, resulting in an increased yield of light oil. See also Turner (U. S. Patent 1,046,683, Dec. 10, 1912) and Noad (U. S. Patent 971,468, Sept. 27, 1910). Hall (U. S. Patent 362,672, Nov. 8, 1887) uses "converting surfaces" of granite. Wilkinson (U. S. Patent 145,707, Dec. 16, 1873) has specified the distillation of petroleum oils with hydrogen.

The French patents to Sabatier, 400,141, and to Haller, Sabatier and Senderens, 376,496, are of interest in this connection.

In studying the effects of catalytic agents upon the decomposition of petroleum oils, 100 grams of coarsely powdered porous earthenware upon which nickel had been reduced in metallic form were impregnated with 10 to 12 grams of the oil, and heated

The British Patent to **Bedford and Williams**, 2520, of 1907, contains probably the first published description of a method of exposing oil to the action of hydrogen by forming the oil in a spray or films in an atmosphere of hydrogen and in contact with a catalyzer of the nickel type. In this manner the patentees state they converted linseed oil into a hard fat solidifying at  $53^{\circ}\text{C}$ . Oleic acid was converted into stearic acid having a melting point of  $69^{\circ}\text{C}$ ., and paraffin wax they state had its solidifying point raised  $3^{\circ}\text{C}$ . by the treatment.

A peculiar manner of treatment has been shown by **Schworer**,\* which will be made clear by Fig. 7. The receptacle *A*, which is heated

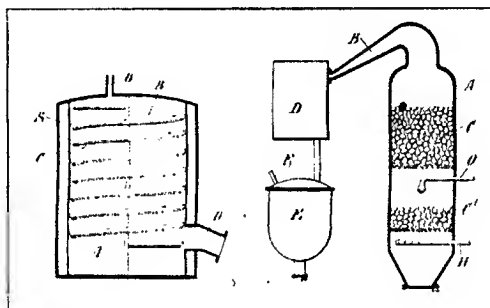


Fig. 7.

Fig. 8.

by the steam jacket *S*, is provided with what Schworer calls a helical pan, shown at *B*. The underside of the pan carries a layer of nickelized asbestos. *O* is an inlet for oil and hydrogen, and *D* an outlet for the treated material.

Schworer states that he first mixes fatty acid and hydrogen by atomizing the oil with a jet of superheated steam in the presence of hydrogen and conducts this mixture through the pipe *O*, into the chamber *A*. The temperature maintained in the apparatus is from

at regulated temperatures from  $180^{\circ}$  to  $500^{\circ}\text{C}$ . in a current of hydrogen. The gases were collected and analyzed, while the distillates were compared with those obtained under parallel conditions, but without the presence of the catalytic agent. No lowering of the vapor pressure appeared to be caused by the catalytic action. Various proportions (according to the partial pressure, temperature, etc.) of hydrogen, methane, ethane and heavy hydrocarbons were produced under the influence of the catalytic agent, while the distillates were of quite different character from those yielded by the oil alone. Ubbelohde and Woronin, *J. S. C. I.*, 1911, 1242; *Petroleum* 1911 [7], 9.

\* U. S. Patent 902,177, Oct. 27, 1908.

250° to 270° C. Vapors of oleic acid come in contact with the layer of catalyzer on the underside of the helical pan and are converted into stearic acid. The product collects, more or less, in the gutter of the helical pan and is removed at *D*.

The repeated caution given by Sabatier to bring in contact with the catalyzer only the *vapors* of the material, doubtless led Schwoerer to devise this form of apparatus.

**Bedford**, presumably with the same caution of Sabatier in mind, discloses, in U. S. Patent 949,954, of Feb. 22, 1910, a process which also has to do with vaporization of the oily material. Fig. 8 shows the Bedford apparatus. A still or tower *A* carries two beds of catalyzer *C* and *C'*. This is said to be preferably nickelized pumice. By means of hydrogen under pressure, oleic acid is sprayed from the pipe *O*, onto the catalyzer bed *C'*. Hydrogen is admitted through the pipe *H*. A temperature of about 200° C. and a diminished pressure of about 50 to 100 mm. is maintained in the still or tower *A*. The vapors of oleic acid mingled with hydrogen pass through the second catalyzer bed *C*, where more or less conversion occurs, then pass to the condenser *D*, and finally collect in the receptacle *E*. *F* is a connection to a vacuum pump.

Neither this process nor that of Schwoerer is broadly applicable to the treatment of glycerides as these cannot be vaporized without undue decomposition.\*

**Erdmann** has taken out a German Patent 211,669, of Jan. 19, 1907, involving passing an oil as spray or mist into a chamber containing nickel catalyzer supported on pumice and the like. Fig. 9 probably indicates one form suggested by Erdmann, who, by the way, does not show any drawings in the patent. The chamber *A* has a rotatable cylinder *B*, which is coated with nickel catalyzer. In the bottom of the receptacle is a quantity of nickelized pumice. Oil enters at *O* and is atomized by hydrogen entering at *H*. The atomized mixture impinges upon the rotating cylinder *B*, then passes through the bed *C*, the oil being drawn off at *D*. The excess of hydrogen is presumably vented in the upper part of the apparatus.

\* Sabatier and Senderens, *Annales de Chimie et de Physique* [8], 4, 335 (1905), state that "Le métal ne soit jamais mouillé par un afflux excessif du liquide que l'on traite, ou à la suite d'un abaissement accidentel de la température du tube." They further say that in the preparation of cyclohexanol and its homologues from phenol or cresol at a temperature but slightly above the boiling points of the latter bodies, sometimes by their condensation, the nickel becomes moistened and immediately becomes almost inactive, due, no doubt, to the surface becoming permanently changed in character by contact with the liquid phenol or cresol.

A second modification (Fig. 10) involves a tower *A*, filled with catalyzer *C*, which may be in the form of nickel supported on coarse fragments of pumice. By the pipe *O* oil is admitted to the chamber in an atomized or finely-divided state. Hydrogen enters by the pipe

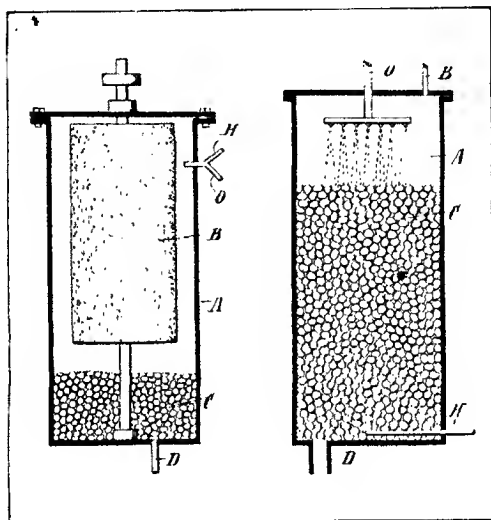


Fig. 9.

Fig. 10.

*H.* Erdmann states that the temperature of treatment should be from 170° to 180° C. The treated oil is drawn off at *D* while the excess of hydrogen passes away at *B*.

In a supplement patent 221,890, of 1909, Erdmann recommends the steam distillation from the reaction chamber of the saturated product under diminished pressure.

**Vereinigte Chemische Werke A. G.\*** make use of a palladium catalyzer precipitated on an indifferent body as a carrier and recommend as carriers finely-divided metals which do not have anti-catalytic properties, also metal oxides and carbonates. Under these circumstances it is stated that one part of palladium is sufficient to convert in a few hours 100,000 parts of oily material to a firm mass. They recommend the use of a hydrogen pressure of two to three atmospheres and a temperature somewhat above the solidification point of the saturated fat. They caution against arsenic, hydrogen phosphide

\* German Patent 236,488, Aug. 6, 1910; also British Patent 18,642, 1911.

and sulfide, liquid hydrocarbons and carbon bisulfide, chloroform, acetone and free mineral acids as being destructive to the activity of the catalyzer.

**Kayser** \* describes a process of treating oil with metallic catalyzer consisting in mechanically agitating the oil and catalyzer in the presence of hydrogen, preferably under pressure. One form of the apparatus indicated by Kayser for this purpose is diagrammatically represented by Fig. 11.

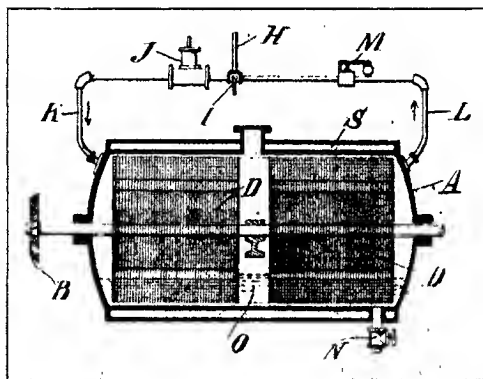


FIG. 11.

Here *A* is a closed horizontal cylindrical vessel in which is a paddle wheel *D*, made up of blades carrying wire gauze. The paddle wheel is rotated by a driving gear at *B*. In the upper part of the tank is an inlet for charging oil and presumably also the catalyzer, the oil being admitted to the tank in an amount sufficient to fill to perhaps one-fourth or one-fifth the entire capacity. Hydrogen is admitted at *H* and passes, by the three-way cock *I*, to the compression pump *J*, going from there to the treating receptacle. At the opposite end of the tank is an exhaust pipe *L*, carrying a blow-off valve *M*, for the purpose of venting the unabsorbed hydrogen. The temperature of treatment is stated to be about 150° to 160° C. Although the claims call for the use of hydrogen under pressure, no working pressures are specified. Fig. 12 shows diagrammatically one form of construction of the screen-covered paddle wheel used by Kayser.

In another U. S. Patent 1,008,474, of Nov. 14, 1911, Kayser sets

\* U. S. Patent 1,004,035, Sept. 26, 1911.

forth the use of an inert pulverulent material such as kieselguhr as a carrier for the nickel catalyzer, he apparently having determined, as did Sabatier and others, that in some cases hydrogenation is more rapid

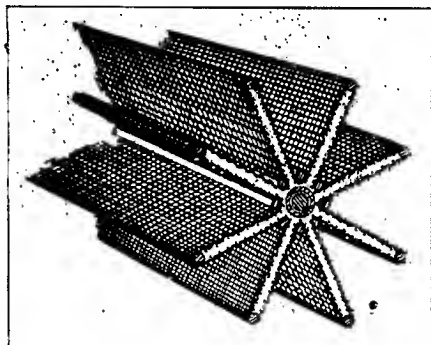


FIG. 12.

or complete when a carrier for the catalyzer is used; and he claims the process of hydrogenating oil involving agitation of a metal-impregnated inert pulverulent carrier (kieselguhr) with a fatty oil in the presence of hydrogen. It is commonly understood that the Kayser process is in operation on a large scale in this country.\*

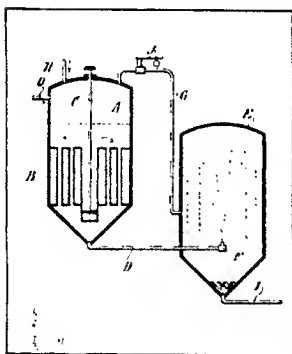


FIG. 13.

Two patents relating to the spraying of oil into a chamber containing compressed hydrogen have attracted some attention abroad. One of these is British Patent 7726, of 1910, to **Testrup**, and the other is to **Wilbuschewitch** which finds its counterpart here in U. S. Patent 1,024,758, of April 30, 1912. Fig. 13 shows the elements of the Testrup process.

Oil and catalyzer are pumped through the pipe *O* into the tank *A*, and hydrogen is admitted by the pipe *H* to furnish a gas pressure of, say, 15 atmospheres. The tubes *B* are

\* The **Kayser** patents are assigned to the Procter and Gamble Co., which concern is a large producer of hardened oil. A product termed "Crisco" is used as a substitute for lard.

heated by steam and the stirrer *C* circulates the oil and catalyzer in the tank *A*, until the oil has become heated and presumably somewhat hydrogenated. The oil is allowed to pass into the adjacent tank *E*, entering this tank by the spray nozzle *F*. Hydrogen gas is admitted to the tank *E* from the tank *A*, so as to afford a pressure of, say, 12 atmospheres in the tank *E*. A series of tanks may be arranged with a constantly decreasing pressure so that the differential pressure enables the spraying of the oil from tank to tank. Testrup states that spraying the material ten or fifteen times is sufficient to bring an oil of an iodine number of 110 down to an iodine number of 50.

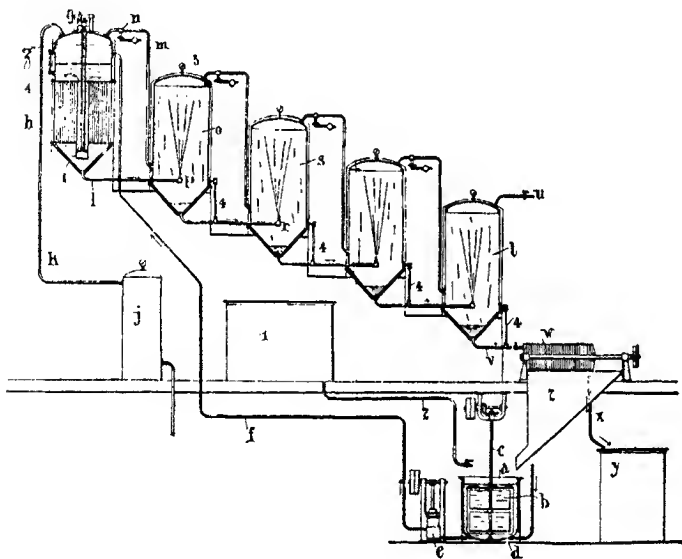


FIG. 14.

According to one form employing the apparatus shown in Fig. 14, and treating cottonseed oil, the oil, mixed with a suitable contact substance, such as finely-divided palladium or preferably nickel, is placed in a vessel *a* provided with a stirring device *b* comprising blades or like elements fixed to a vertical and rotatable shaft *c* within it. The amount of nickel may be about 2 to 3 per cent by weight. This vessel is preferably jacketed as at *d*, and is heated by the passage of heated fluid through this jacket, say to about 160° C. From this chamber the oil is pumped by a pump *e* through a conduit *f* and enters a vessel *g*, which is jacketed and heated by tubes *h*, being also provided with a mixing device comprising a central tube and propeller arrangement *i*. Hydrogen gas is supplied at high pressure from a reservoir *j* through



a duct *k*. The vessel *g* has an educt *l* for the material under treatment at its base and an educt for hydrogen *m* provided with a loaded valve *n*. The duct *m* opens into a vessel *o* into which the oil from the vessel *g* is sprayed by a spray nozzle *p* attached to the end of the duct *l* by the pressure of the gas in the vessel *g*. The oil and catalyst thus exposed to the action of the gas fall into the base of the vessel *o* to be forced by the pressure of the gas therein through a duct to a nozzle *r* in another vessel *s* wherein the operation is repeated. Several such vessels are arranged in this way in cascade, all being jacketed to allow of maintaining the desired temperature. The last vessel *t* is provided with any suitable educt *u* for the gas and an educt *r* for the treated oil and catalyst which is passed to a filter press *w* in which the oil is separated from the catalyst, the former passing by a duct *x* to a reservoir *y* and the catalyst being returned to the vessel *a* for which purpose the chute *z* may be utilized. Should the catalyst have become contaminated with nickel soap it may be purified as by washing with acid. A storage tank for the material awaiting treatment is indicated at 1 with its duct 2 leading to the vessel *a*. Gauges for noting the pressure 3 and the level gauges 4 are also employed. The temperature at which the reaction is conducted is about 160° to 170° C., and the pressure of the hydrogen in *g* may be about 15 atmospheres, in *o* say 12 atmospheres, the difference in pressure producing the spray. The pressure may similarly fall by 3 atmospheres for each vessel. It may

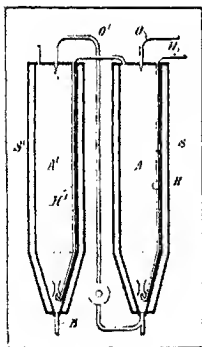


FIG. 15.

be necessary to pass the substance again through the apparatus or to provide several systems of heaters and spraying devices in series in order to obtain the desired result but by this process the desired number of repetitions can be carried out rapidly.\*

Even such a number of treatments are stated to require only about 30 minutes or less and the number of treatments would depend largely on the activity of the catalyst employed.

The Wilbuschewitch Patent itself details a rather complicated system, and Fig. 15 shows only what appears to be the essential features of the treating apparatus. Several tanks or autoclaves are connected as shown at *A* and *A'*, oil entering the top of the tank *A* by the pipe *O*, to form a spray which in descending

meets an upward current of hydrogen entering by the pipe *H*. The oil is drawn off through the pipe *O'*, and sprayed into the tank *A'*. This time it meets a current of hydrogen represented by the excess of hydrogen coming from the tank *A*. The treated oil is drawn off and may be centrifuged to remove the catalyzer. A pressure of nine atmospheres is recommended and the pressures may be varied in the different tanks.

\* Swedish Patent 992, May 27, 1911 (Techno Chemical Laboratories, Ltd.), on the hydrogenation of organic substances involving a process which essentially consists in mixing catalyzer with the substance to be treated and in subjecting the mixture in an atomized or finely-divided condition to the action of hydrogen, leads

Of the Willbuschewitch process **Goldschmidt** \* states that the high hydrogen pressures employed enable the reaction to take place quickly at temperatures between  $100^{\circ}$  and  $160^{\circ}$  C., so that the fat is not likely to be injured by the temperature to which it is subjected. It should be stated that several years previous to the date of the Willbuschewitch patent, Ipatiew had noted and carefully studied the action of increased pressure.

**Bedford** and **Williams** have brought out an interesting process represented by U. S. Patent 1,026,339, of May 14, 1912. Fig. 16 shows the apparatus indicated by Bedford and Williams for carrying out the process. Oil is placed in the receptacle A, which is heated by

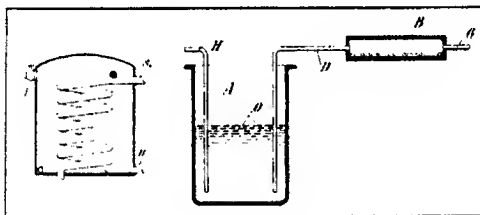


FIG. 16.

FIG. 17.

a steam coil *S*. Metallic oxide catalyzer is added, about 1 per cent being recommended, and hydrogen and oxygen or air is introduced by the pipe *H*. As a catalyzer, nickel oxide † is recommended and instead of the customary hydrogenating temperatures of  $150^{\circ}$  to  $170^{\circ}$  C., a temperature of about  $250^{\circ}$  C. is employed. While hydrogen alone may be used for the purpose, the inventors recommend and claim treatment of the oil with a mixture of hydrogen and oxygen to form hydroxy fatty acids or their glycerides.

A process for the conversion of fatty acids or their glycerides into saturated bodies in which a finely-divided metal oxide serves as a catalyzer is described by Bedford, Williams and Erdmann, ‡ and the reaction is carried out under pressures ranging from atmospheric pressure up to but not exceeding 20 atmospheres. Nickel oxide is especially recommended as the catalytic material.

the editor of *Chemiker Zeitung* (*Chem. Zeit. Rep.* (1913), 320) to make the comment that it is somewhat questionable according to other investigations which have been made in this direction, whether this process is practical for the manufacture of edible fats and the like.

\* *Chem. Ztg.*, 1912, 945.

† Previously used by Ipatiew.

‡ *Siefen. Ztg.*, 1913, 1413.

**Shukoff** \* claims the process of hydrogenating oils by means of nickel derived from the decomposition of nickel carbonyl. The carbonyl may be obtained from reduced metallic nickel by passing carbon monoxide over it at a low temperature. Nickel carbonyl is soluble in oil and is very readily taken up by gases. On heating to a temperature of 200 degrees or so, the carbonyl is decomposed, setting free, in a nascent state, metallic nickel which acts as a catalyzer. Shukoff makes use of this reaction of nickel carbonyl by the method indicated by Fig. 17. Carbon monoxide is passed by the pipe *G* into the tube *B*, containing finely-divided nickel and the nickel carbonyl formed is conducted to the oil *O*, which is heated to about 180 degrees. After sufficient nickel catalyzer has formed in the oil, the carbon monoxide stream is cut off, the temperature raised to 220° or 240° C., and hydrogen gas introduced by the pipe *H* to bring about hydrogenation.

Schukoff states if nickel carbonyl in a gaseous condition or a nickel-carbonyl-containing gas mixture is conducted into the material to be reduced, which may be either in a molten condition or in solution in a suitable solvent, it is found, when the temperature advances beyond the temperature of dissociation of nickel carbonyl, that metallic nickel in an extremely finely-divided state is separated and that the division obtained in this way is so fine as to cause the reaction mixture to appear black in color, and the separated nickel settles only after very long standing. As an example: Into 8 kilos of cottonseed oil warmed to 180° C. a slow stream of 400 liters of carbon monoxide is passed, which carbon monoxide has previously passed over a long layer of metallic nickel warmed to about 60° C.; finely-divided active nickel separates in the oil; the stream of carbon monoxide is then interrupted, the temperature raised to 230° to 240° C., and hydrogen as a slow stream is run into the mixture during a period of five to six hours in an amount of 3000 liters. The reaction mixture on cooling is completely hard; by filtration the nickel can be removed and the product eventually converted into stearic acid.

**Day** has taken out U. S. Patent 1,004,632, of Oct. 3, 1911, supplementing his earlier patent on the treatment of hydrocarbon oils with hydrogen. In the present instance tubes packed with catalyzer are placed in an oil still in such a manner that vapors from the oil may pass through the catalyzer tube in conjunction with hydrogen while being superheated by exterior contact of the tubes with boiling oil.

An English Patent, 23,997, of 1909, to **Phillips** and **Bulteel** claims,

\* German Patent 241,823, Jan. 18, 1910. See also H. Kamps, Belgian Patent 246,975; Seifen. Ztg., 1912, 1339. U. S. Patents, 738,303, 777,848 and 943,627 are of incidental interest.

to convert mineral oils into oils of lower specific gravity by heating with hydrogen in the presence of nickel or other catalytic agents. They state that the mixture of oil, gas and catalyst may be blown into a heated cylinder and the jet given a gyratory motion either by means of a nozzle revolving about its axis or by injecting the mixture tangentially to the periphery. In the latter case they state that the cylinder may have an axial core.\*

The firm of **H. Schlinck & Co.**, of Hamburg, Germany,† hydrogenate oil by passage through a centrifuge, the drum of which carries a porous lining supporting palladium catalyzer which offers a frictional resistance to the passage of the oil. Fig. 18 shows a centrifugal drum *a*, which is closed at the top and can be heated. Oil and hydrogen are introduced through the pipe *b*. Openings are provided in the walls of the drum in which is placed rough or porous material covered with precipitated palladium. Several drums may be arranged in series

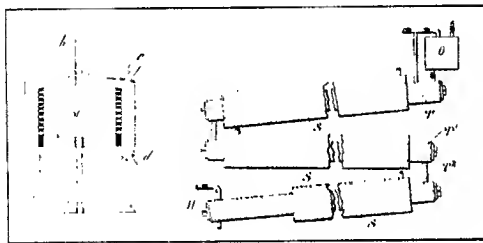


FIG. 18

FIG. 19.

\* In the treatment of hydrocarbons with superheated steam Hausmann and Pilot (German Patent 227,178, 1909) recommend as catalyzers the oxides of iron, lead, cerium and manganese, also iron sulfate and calcium manganite. Richter (German Patent 240,760, 1910) makes use of active carbon as a carrier for oxygen in the treatment of petroleum and other oils. Laffer (British Patent 2328, 1912) distills petroleum oil under pressure while circulating an inert gas through the body of oil in the still. Laffer mentions hydrogen among the inert gases suitable for the purpose. Lamplough (British Patent 19,702, 1912) proposes to effect reaction between petroleum oil and water by passing a mixture of the vapors of these bodies over rods of metallic nickel while subjecting the vapors to a pressure and to a temperature approaching a dull red heat. From 20 to 60 parts of water are used to 100 parts of oil. Dibdin and Woltereck (British Patent 19,152, 1901) bring a mixture of superheated steam and petroleum oil into contact with iron, copper and other metals maintained at a bright orange heat to effect the simultaneous decomposition of the steam and hydrocarbon. They also mention (British Patent 26,666, 1905) the use of "protoperoxide" of iron.

† British Patent 8147, 1911. The corresponding patent in the United States is 1,082,707, Dec. 30, 1913.

through which the oil may be caused to progress until sufficiently hydrogenated.

Ellis \* uses a stationary catalyzer, filling tubes with the material in granular form and allowing oil to flow through the tubes while passing hydrogen in an opposite direction. Fig. 19 shows a three-section apparatus with the catalyzer tubes  $T$ ,  $T^1$  and  $T^2$ , heated by the jackets  $SS$ . Oil from tank  $O$  flows through the apparatus while hydrogen, admitted by the pipe  $H$ , passes through in an opposite direction. The arrangement permits of differential heating so that, for example, the oil may be heated to a temperature corresponding to its particular degree of hydrogenation at any given point, enabling a hydrogenated product free from "burnt" odor to be obtained. Fig. 20 shows a vertical form of apparatus, the catalyzer being shown at  $C$  in the tube  $A$ .

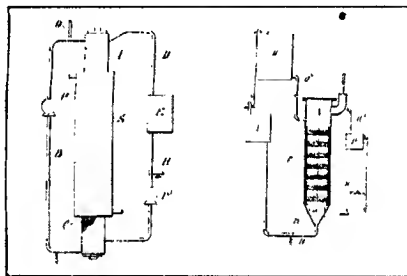


FIG. 20.

FIG. 21.

Oil is introduced by the pipe  $O$ , and passes into the tube or cylinder  $A$ . The pump  $P$  causes oil to circulate from the top to the bottom of the apparatus through the pipe  $B$ . Hydrogen gas admitted at  $H$  is pumped into the bottom of the cylinder  $A$ , and the excess is withdrawn at the top by the pipe  $D$ , passing through the drier  $E$ , and back into the treating cylinder. Oil may be continuously fed through the pipe  $O$  in the upper part and the treated product withdrawn at the same rate at the lower part of the apparatus.

In another form† of the apparatus, the catalyzer is placed in trays or baskets as shown by Fig. 21 at  $C$ . The oil travels in a cyclic path downward through several layers of catalyzer, and hydrogen gas passes in an opposite direction. Separation of the catalyzer in layers in this manner enables the hydrogen to pass more uniformly through the

\* U. S. Patent 1,026,156, May 14, 1912. See also U. S. Patent 1,052,469, Feb. 11, 1913.

† U. S. Patent 1,040,531, Oct. 8, 1912.

catalyzer bed. If the catalyzer forms a bed of considerable depth and width, the gas in taking the path of least resistance is liable not to come in contact with some parts of the bed.

The activity of a properly made catalyzer is oftentimes surprising. In the case of a stationary catalyzer the author has noted instances of hydrogenation where oil is converted into a hardened fat by scarcely more than momentary contact with the catalyzer.

Fig. 22 shows a photograph of a small laboratory apparatus for testing catalyzers, consisting of an inclined tube containing the catalyzer and carried in a heating jacket. Oil is admitted at the right and hydrogen at the left-hand end. Fig. 23 shows the catalyzer tube at the right from which extends a horizontal tube supplying hydrogen to the catalyzer tube.



FIG. 22.

When using a new type of catalyzer the author started to pass oil through the catalyzer tube and found hydrogen to be absorbed so vigorously by the oil that instead of passing off through an oil seal at the lower end of the inclined catalyzer tube, the oil, curiously enough, was impelled against the strong current of hydrogen passing through the horizontal tube, rushing through it to the point indicated by the hand of the operator (Fig. 23) and there solidifying, actually being well hydrogenated from its brief passage through the apparatus. A

peculiar feature was the advance of the oil from the tube containing catalyzer far into the tube through which only the hydrogen was entering the apparatus. The travel of the oil along the hydrogen-supplying pipe in opposition to a rapid current of hydrogen indicates the possibility of hydrogenating in a very short time, provided a catalyzer of a high degree of activity is secured.

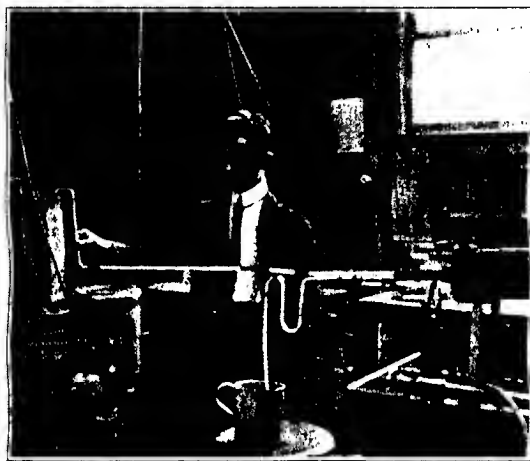


FIG. 23.

On the other hand, some catalyzers of the nickel and cobalt type when first brought into contact with oil and hydrogen show for a time a certain degree of sluggishness, but after a period, their activity rather suddenly augments and thenceforth remains apparent for a long period. This sluggishness should not be confounded with the seeming initial inactivity in the hydrogenation of oils containing considerable linolein or other highly unsaturated bodies. In such cases the rate of "hardening" (increase in melting point) is slow at first and later progresses more rapidly. Hydrogenation, in some cases at least, apparently proceeds selectively with initial formation of olein from linolein. Later the olein is transformed into stearin with the observed more rapid increase of titer.\*

\* Mailhe (Rev. gen. des Sciences, 1913, 653) makes note that he has seen cottonseed oil hardened to a high titer by twenty minutes exposure to hydrogen and catalytic material.

*Marcusson* and *Meyerheim* \* have reached the conclusion that fish oil (tran) does not hydrogenate selectively or by stages, that is to say, the more highly unsaturated components do not largely take up hydrogen before olein becomes converted into stearin. A certain percentage of the highly unsaturated fatty acids remain even after a large proportion of the oleic acid has been transformed into stearic acid. The inner iodine number (iodine number of the liquid fatty acids) of a sample of hardened tran was found to be 107, which result led to the foregoing conclusion.

*Ellis* † effects a constant circulation and contact of the hydrogen gas in accordance with the method shown by Fig. 24. The tank *A* contains a body oil *O*, the space above the oil being filled with hydrogen under any suitable pressure. The tank is heated by the jacket *S*. A pump *P* withdraws the hydrogen from the upper part of the tank and impels it through the pipe *D* into the lower part of the tank. The catalyzer is added to the oil when the proper temperature is reached and the constant bubbling of a stream of hydrogen through the oil causes intimate contact between the reacting elements. After the

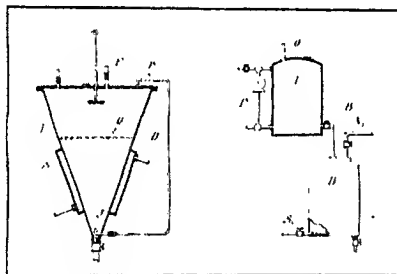


FIG. 24.

FIG. 25.

operation is completed, the porous plate, fastened to a movable stem in the upper part of the tank, may be depressed to fit into the bottom of the conical base so that when the oil is withdrawn a good portion of the catalyzer remains without exposure to the air and may be used with perhaps a small addition of fresh catalyzer for the treatment of a succeeding charge of oil.

In U. S. Patent 1,043,912, *Ellis* hydrogenates oil (Fig. 25) in the autoclave *A*. The pump *P* circulates hydrogen gas through the oil. The treated product is run into the deodorizer *D*, where it is treated

\* *Zeitsch. f. angew. Chem.* 1914, No. 28, 201.

† U. S. Patent 1,059,720, April 22, 1913.



with superheated steam under diminished atmospheric pressure until the oil is freed from noxious gases or vapors. While the deodorization of ordinary cottonseed oil, for example, requires a temperature from 200° to 300° C. and a vacuum of down to one or two inches mercury, the deodorization of the hydrogenated cottonseed oil does not necessarily require as high a temperature and the vacuum "pulled" may be considerably less.

Contrary to the opinion entertained by many it does not appear needful to violently agitate the catalyzer primarily for the purpose of contacting it with hydrogen. Once the catalyzer is wetted with the oil there can no longer be any actual contact with the gas. Hydrogen reaches the catalyzer seemingly only through solution in the oil. The forces of adhesion effectually seal the catalyzer surface from the gas, and no measure of agitation by ordinary mixing apparatus will dislodge the film of oil. Of course, agitation secures the rapid replacement of more saturated by less saturated portions of the oil, but this replacement, under certain conditions, may proceed rapidly, simply by diffusion.

The direct pumping of hot hydrogen gas, especially if the latter is under considerable pressure, offers some difficulties, and the apparatus shown in Fig. 26 is designed to effect a circulation of the gas by inductive effect.\* The tank 1 carries an inductor 2 through which is forced oil propelled by the pump 3. The passage of the oil through the inductor causes hydrogen, which is supplied to the upper part of the tank, to be drawn into the central vertical pipe and carried with the oil to the bottom of the tank when the gas bubbles through the main body of oil. Thus the oil which is being treated is made use of to circulate the gas.

Another type of apparatus† involves circulating hydrogen gas by means of an oil sealed pump which may be so arranged as to permit the return of any hydrogen escaping through the stuffing boxes. Fig. 27 shows this apparatus. 1 is an oil treating tank with gas outlet 2, communicating with a drier or purifier 3. From the lower part of the latter a pipe leads to the pump 4 which is enclosed by the housing 5, the space between pump and housing being filled with oil. The pump discharges into the lower part of the tank through the gas distributor 6. A connection 7 from the upper part of the housing to the tank provides a vent for gas escaping from the pump.

In hydrogenating oleic acid in a vaporized state Shaw‡ obtained

\* U. S. Patent to Ellis, 1,059,720, April 22, 1913.

† U. S. Patent to Ellis, 1,071,221, Aug. 26, 1913.

‡ Seifen. Ztg., 1912, 713.

some rather curious results. As a hydrogenating apparatus Shaw used a glass tower, holding catalyzer, the latter being prepared by putting fragments of pumice into a 50 per cent solution of nickel nitrate. The pumice was heated to a red heat in order to convert the nitrate

to the oxide and the process repeated in order to get a good coating. The material was then placed in the glass tower and reduced by hydrogen at about 300° C., reduction taking place in 2 to 3 hours. The tower was heated in an oil bath.

Oleic acid was supplied from a distilling flask which was con-

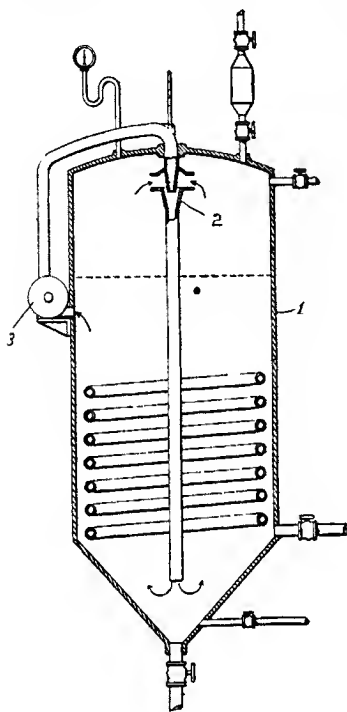


FIG. 26.

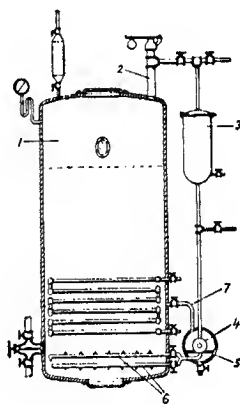


FIG. 27.

nected with the tower by gas-tight piping. In the flask was inserted a tube through which hydrogen could be introduced. The hydrogen was generated in a Kipp apparatus, passed through wash bottles containing nitric acid and sulfuric acid, and finally through a "U" tube containing fragments of caustic potash. From the tower a delivery tube extended to a receiver which was connected with a manometer and an air pump. The temperature of the oleic acid was maintained a few degrees above the boiling point of the acid, or about 300° C. In this way the catalyzer was never wetted with the liquid acid, but came in contact only with the gaseous acid which distilled over from the flask. The reaction product was condensed in the receiver.

The degree of reduction was determined through the iodine number with the following results: the iodine number of oleic acid employed was 79. When distilled under a pressure of 100 mm., the resulting product had an iodine number of 75, which corresponds to a reduction of 5 per cent. This partially reduced product under a pressure of 100 mm. was distilled through the catalyzer, and the product obtained had an iodine number of 74.8, practically identical with the previous value. In reviewing this unfavorable result it was concluded that the catalyzer was poisoned and its activity lost. To test this out a fresh portion of oleic acid was distilled through the catalyzer. Again a reduction of 5 per cent occurred, which indicated that the catalyzer was not poisoned.

Distillation at 150 mm. was then tried, giving a reaction product having an iodine number of 68 to 70. When this product was distilled again at 150 mm., the same iodine number was obtained. A pressure of 200 mm. was then employed and the reduction was 20 per cent, while a second distillation at 200 mm. did not increase the amount reduced.

These results suggested the possibility of an equilibrium between stearic acid, oleic acid and hydrogen, and that the reduction degree which Shaw found varied from pressure to pressure was constant for any one pressure. If this conclusion were correct, then the equilibrium should be reached from the opposite end, namely through distilling stearic acid in the presence of hydrogen. In order to see whether this were possible stearic acid was treated in exactly the same way as the oleic acid by distilling through freshly prepared catalyzer. As a result of the test it appeared that stearic acid experienced no change in iodine number which apparently excluded the idea that conditions of equilibrium were involved.

Shaw's observations that by repeated distillation of oleic acid no further reduction occurs was not to be explained on the ground of fractional distillation of the partially reduced product, for the entire contents of the flask were distilled through the catalyzer, and furthermore the boiling point of stearic acid differs very little from oleic acid, so Shaw is at a loss to explain the cause of this peculiar behavior after finding it not due either to the existence of equilibrium or fractional distillation.

An investigation was made to determine what influence length of time had on the progress of reduction. The same apparatus was used. Oleic acid was distilled under diminished pressure and the temperature of the oil bath maintained at 275 degrees, while small quantities of the acid were distilled over in definite time intervals and the iodine number determined.

The following is the result:

2 hours	Iodine No. 67	M. P. 23°
3½ hours	Iodine No. 62	M. P. 33°
5 hours	Iodine No. 60	M. P. 37°
9 hours	Iodine No. 45	M. P. 50°

Shaw also determined the effect of pressure considerably above atmospheric and found:

With pressure of 5 atmos;	temp. 250° C;	Iodine No. 77
With pressure of 25 atmos;	temp. 250° C,	Iodine No. 64
With pressure of 50 atmos;	temp. 250° C;	Iodine No. 52

by which he concludes that the reduction progresses in proportion to the increase in pressure.\*

In the decomposition of fats, oils and waxes into fatty acids and alcohols by aromatic sulfonated fatty acids, the fats or fatty acids used in preparing the latter, according to **Connstein** and **von Schonthan**, are reduced before sulfonation, either by catalytic processes or by electrolysis.† For example, castor oil is hardened by treatment with hydrogen, using palladium catalyzer; equal parts of the hardened product and naphthalene are mixed and to the mixture twice its weight of sulfuric acid of 66° Baumé is added, avoiding an increase of temperature above 20° C.

The reaction mixture is stirred until homogeneous and is then poured into somewhat more than its own weight of water. The oily layer which separates is filtered and is then ready for use. An illustrative example of the process by the patentees calls for treatment of 1000 parts of palm kernel oil, 300 parts of water and 2 parts of the fat cleavage compound for 6 to 8 hours with dry steam. After separation of the two layers the lower layer or glycerine water is concentrated in the customary manner while the upper layer consists of fatty acids.

According to **Steffan** ‡ this fatty cleavage reagent has been placed on the market under the name of "**Pfeilring**." § **Steffan** comments on the discoloring action of the Twitchell process on some fats and oils among which he mentions certain grades of tallow, soya bean oil and fish oil, the coloration of whose fatty acids when produced by the

\* Sabatier notes in his book on Catalysis, Paris, 1913, 78, that the vapors of oleic acid entrained by a strong current of hydrogen and passed over nickel heated to 280° to 300° C. are rapidly transformed into stearic acid, and the same thing occurs with the isomer elaidic acid. (See Ann. Chim. Phys. (8), 16, 73, 1909.)

† British Patent 749, Jan. 10, 1912, Vereinigte Chem. Akt. Ges.

‡ Seifen. Ztg., 40, 550.

§ "Pfeilring" cleavage composition from the patent standpoint is critically discussed by Esch (Chem. Rev. u. d. Fett u. Harz Ind. (1913), 295).

Twitchell process being so dark that when made into soaps the color of the product leaves much to be desired.

Fat cleavage reagent prepared with the hardened oil is claimed to produce a much lighter fatty acid. The rate of saponification with the hardened oil product Pfeilring is approximately that of the Twitchell reagent. Using equal parts of the two reagents under like conditions the following results were obtained:

	5 hours, per cent	23½ hours, per cent	34 hours, per cent
Twitchell reagent	37 23	83 31	88 94
Pfeilring reagent	36 92	80 18	88.69

These results indicate for Pfeilring a rate of cleavage slightly less than that of the Twitchell reagent, but it is brought forward by the supporters of Pfeilring that, the latter reagent being in itself very light colored, while the Twitchell reagent has a blackish cast, the proportion of the latter which may be used is limited by the required color of the resulting fatty acids, but that Pfeilring may be used in larger proportion without the danger of discoloration and hence the rate of cleavage may be increased by using a larger quantity of the reagent while the reaction may be carried more nearly to completion, that is to 95 per cent and over, without the discoloration sometimes observed in the Twitchell process.

In response to a critical discussion of the properties of soaps made with hardened oils \* **Sudfeldt Brothers** state † that for several years they have been splitting large quantities of hardened whale oil by the Twitchell process and converting the fatty acids into soap and have found these fatty acids to be of good color and the soaps prepared from them to be in no wise lacking in color. The sharp odor noticed in the neutral fat is not lost by the splitting operation and also appears in the finished soap.‡

Reference has been made to the work of **DeHemptinne** on the effect of electrical discharge in causing the addition of hydrogen to unsaturated oils. Later work by this investigator § furnishes additional data on this interesting reaction. The formation of stearin by the action of an electric discharge on commercial olein in an atmosphere of hydrogen was studied on both a small and large scale. The apparatus employed on a large scale consists of a rotatable horizontal axle

\* Seifen. Ztg. No. 25, 1912.

† Seifen. Ztg. (1912), 720.

‡ Sudfeldt & Co. contend in favor of the Twitchell reagent; Seifen. Ztg. (1913), 613. See also Seifen. Ztg. (1914), 311, 338 and 392.

§ Bull. Soc. Chim. belg., 26, 55.

bearing a large number of thin, parallel, vertical iron plates separated by glass plates, the former being connected together alternately on opposite sides. The whole is mounted in an air-tight iron drum which is partially filled with olein and into which hydrogen is introduced; the odd numbers of the iron plates are connected with one pole of a high-potential alternator and the even numbers with the other pole. When the axle is rotated, the electric discharge passes through a thin layer of olein which constantly wets the plates. The glass dielectric may be arranged so as to contact with one or both faces of the iron plates (the free space in the latter case being between the dielectrics) or the dielectrics may be separated from both faces of the iron plates. The capacity of the largest apparatus constructed was about 1000 pounds. Apart from the construction of the apparatus the yield is influenced by the current density, the frequency of the current, gaseous pressure, temperature of the liquid and the distance between consecutive iron plates. If the reduction is not pushed beyond a point corresponding to a 15 per cent decrease in the iodine number, there is a complete parallelism between the decrease in the iodine number, increase of melting point and absorption of hydrogen. The variation of the iodine number or the increase of the melting point per unit of electrical energy employed is taken as a measure of the transformation effected. A proportionality between the quantity of substance transformed and the intensity of current does not always exist. For a given intensity of current the quantity transformed reaches a maximum for a definite distance of electrical discharge; this maximum varies with the pressure. In order to obtain a satisfactory reaction the current must act simultaneously on both liquid and gas. Prolonged action of the current causes polymerization and the reactions become quite complicated. The apparatus can be used for deodorizing fish oil, as the unsaturated compounds of this oil take up hydrogen under these conditions. Because of the gradual polymerization produced the method is suggested as applicable for thickening mineral oils or mixtures of mineral oils with animal or vegetable oils. Molecular weights as high as 2500, as determined by the ebullioscopic method, were obtained. The viscosity of these polymerized oils varies less with the temperature than does that of the pure mineral oils; the coefficient of friction of the former is also stated to be less.

Apparatus patented by Hemptinne\* is of the following character: A series of parallel rotatable metal plates, with discs of insulating material between adjacent plates, is arranged within a fixed casing or within a vessel that rotates with the plates on a horizontal axis.

\* British Patent 7101, April 4, 1905.

Alternate metal plates are connected to one pole, and the remainder to the other pole of a source of electric current, in order to establish a silent electric discharge between the plates. The latter are partially immersed in the absorbing liquid, which is carried around by small troughs attached to the casing and delivered on to the upper portions of the plates, so that a thin layer of liquid is maintained on the plates, and the gas to be treated is thus brought into intimate contact with the liquid. An electro-magnetic device, working automatically, maintains a constant pressure of gas in the apparatus during the absorption.\*

A process for the production of neutral hydrogenated fats from raw material containing fatty acid involves hydrogenating the oil in the presence of glycerine under which condition the fatty acids are claimed to be converted into glycerides.†

With an apparatus as shown in Fig. 28, Ellis ‡ hydrogenates by passing a current of oil through a rotary drum containing catalytic

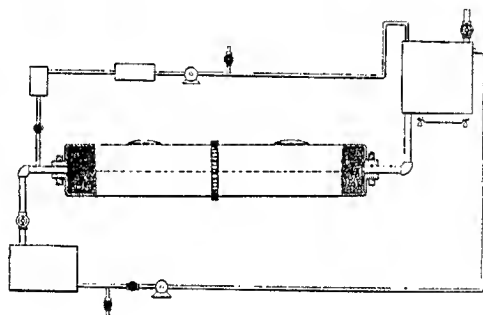


FIG. 28.

material supported on coarse fragments of pumice, so that on rotation of the drum the catalyzer moves in a direction substantially transversely to the direction of the oil current. Hydrogen may be passed through the drum as a counter-current. A given quantity of oil may be circulated in this manner until hardened to the requisite degree.§

\* The application of the electric current in the industry of oils and fats has been reviewed by Buttlar (*Chem. Rev. u. d. Fett und Harz Ind.* (1912), 97) who discusses its use in the transformation of liquid oils into solid fats, also in the bleaching of oils.

† *Seifen. Ztg.* (1913), 263.

‡ U. S. Patent 1,052,469, Feb. 11, 1913.

§ In U. S. Letters Patent 1,095,144 of April 28, 1914, to Ellis a process is set forth for hardening oils which involves the movement of oil and catalyzer in a direction transverse to that of the hydrogen current.

## CHAPTER II

### METHODS OF HYDROGENATION—Continued

**Utescher** \* treats oils with hydrogen in presence of a finely-divided catalytic agent, and at the same time the material is subjected to the action of a silent electric discharge.† In a description of the process, it is stated that the "silent discharge" is prevented from coming into actual contact with the fatty substance, only chemically active rays (e.g. from a mercury vapor lamp) being utilized. It is also stated that the process may be effected by allowing the rays to impinge on the surface of a catalytic substance, which may be used in the form of plates.‡

The joint application of a catalytic and an electric discharge is claimed to give a greater effect than either agent singly.§

Some observations on the effect of ultra-violet light on catalytic action have been made by **Farmer and Parker** || which indicate that on colloidal platinum, at least, the ultra-violet light exerts a retarding influence on the rate of catalytic change. Colloidal platinum was prepared by the Bredig method, i.e., by producing an arc between platinum electrodes under distilled water. Hydrogen dioxide was used as a measure of catalytic activity. The colloidal platinum was exposed to the ultra-violet light and samples were drawn from time to time in order to get exposures of varying lengths, the samples being introduced into hydrogen peroxide placed in an apparatus shown in Fig. 29. The inclined tube of this apparatus was completely filled with dilute hydrogen peroxide solution and a bent delivery tube arranged to collect any liquid displaced. As colloidal platinum breaks

\* British Patent 20,061, Sept. 3, 1912.

† Hydrogen activated by actinic rays is used for oil hardening (Seifen. Ztg. (1913), 1298).

‡ In this connection it is noted that the text of the Utescher specification of German Patent 266,662 of 1912 appears in Chem. Rev. u. d. Fett u. Harz Ind. (1913), 308.

§ Seifen. Ztg. (1913), 851. F. Gruner, French Patent 453,664, Jan. 27, 1913. Oils or fats are subjected to the action of a silent discharge of an electric current of very high tension and frequency. Currents of high potential (50,000 to 100,000 volts) and high frequency are employed.

|| Jour. Am. Chem. Soc. (1913), 1524.



down hydrogen dioxide yielding oxygen, the evolution of the gas and consequent displacement of liquid enabled the rate of decomposition to be measured.

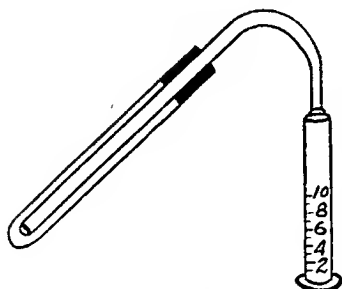


FIG. 20.

the platinum to be precipitated out of solution as a black flocculent material. After such a precipitation it was in the form of large mossy clusters.

While no observations were made with respect to the hydrogenation of oils under these conditions, in view of the action of ultra-violet light on solutions of colloidal platinum, it would appear that exposure thereto may be expected to modify the rate of reaction in the hardening of oils.\*

A process of hydrogenating oils involving exposure of the oil as a thin film on a web carrying catalytic material has been proposed by Walter.† Fig. 30 shows one form of apparatus described by Walter for carrying out this reaction. *A* is a closed vessel in which is placed a belt or web

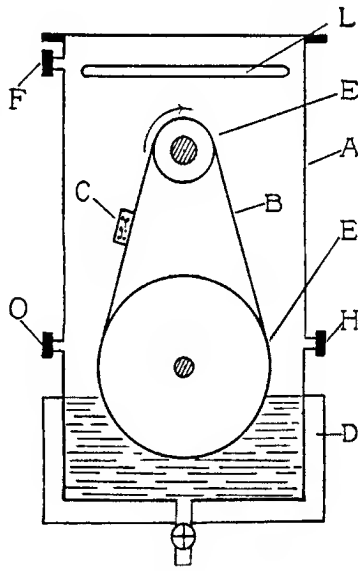


FIG. 30

*B* carrying catalytic material. The belt may be made of asbestos or cotton cloth and may be impregnated with platinum, iridium,

\* Some preliminary experiments by the author point to a reduction in the iodine number of cottonseed oil when exposed to ultra-violet light in an atmosphere of hydrogen.

† *Soilton, Zita* (1912) 442

nickel or other catalytic material. The belt is carried on rollers *E*, one of which dips into the oil. Catalyzer also may be carried in the container *C* attached to the belt *B*. *D* is a steam or water bath. *H* is an inlet and *F* an outlet for hydrogen. *O* is an inlet for oil.

Two other types of apparatus are described: one consists of an upright stationary cylinder jacketed for about one-half the distance. The interior has a shaft with 4 arms upon which the catalyzer is carried and revolved through the liquid and gas. A bucket arrangement is also attached to the shaft to throw liquid upon the catalyzer. Another type consists of a jacketed horizontal cylinder with a rotating shaft supporting arms for carrying the catalyzer. (Figs. 31, 32 and 33.)

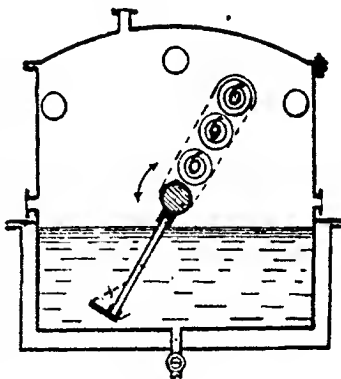


FIG. 31.

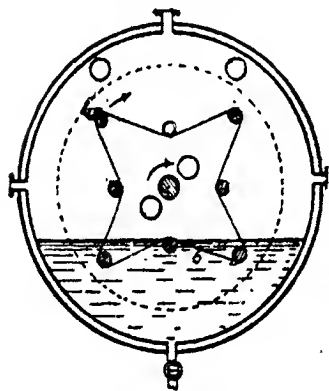


FIG. 32.

The operation may be carried out with the aid of chemically-active light for which purpose a lamp-lighting system of actinic character

is shown at *L* positioned in the receptacle *A*. Walter lays great stress on the rapid absorption of hydrogen by oil or other material exposed in this manner in thin films. He states that although the film of oil on the belt covers the catalyzer, and in consequence one would expect the reaction to be hindered by the sealing effect of such a film, yet the liquid and gas react very quickly with one another. The solubility of the gas in the liquid, as well as the physical properties of the latter, he states, do not appear to play any essential

part, for the sparingly soluble hydrogen exerts its reducing action apparently just as quickly in a thinly-fluid alcoholic quinine solution as it does in a viscous fish oil.

Walter recommends passing the oil through a series of receptacles

containing catalyzer attached to a belt as described or to an agitator arm, the arrangement being such that the oil first enters the receptacle

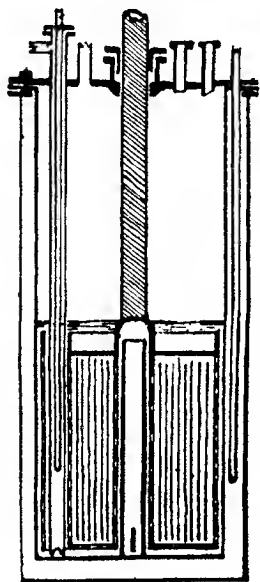


FIG. 33.

which contains the weakest or more nearly spent catalyzer and after short treatment passes to the next container and so on until finally it reaches the last receptacle where the most active catalyzer is employed.

In connection with the above it may be stated that Walter has been granted German Patent 257,825, of July 27, 1911, which, in brief, has to do with the production of chemical reactions between liquids and gases under the influence of a contact substance or of chemically-active rays. Porous or roughened bodies, which may serve as contact substances, are supported on movable carriers and are caused alternately to dip into the liquid and then rise into the gas above the liquid, so as to bring fresh quantities of the liquid continually into contact with the gas, over a large surface. Several reaction chambers through which the gas and liquid pass in a definite order are preferably used. In some respects this resembles the process

of Kayser previously discussed.

**Birkeland and Devik** \* employ a form of apparatus which permits of forcing a mixture of oil and catalytic agent downwards through a nozzle into an atmosphere of hydrogen, filling the space above the bulk of the oil, which is contained in an autoclave. The hydrogen is drawn into the oil jets by injector action and subsequently rises in small bubbles through the body of oil. The process is preferably carried out under a pressure of 10 to 15 atmospheres and at a temperature of about 150° C. Sudden reduction of the pressure is claimed to promote the hydrogenation of the oil.

**Brochet** † treats unsaturated compounds as a class, by hydrogen, in the presence of a catalyst. Hydrogen or a gaseous mixture containing hydrogen is passed into the substance to be treated, either in the liquid form or in solution or suspension, in presence of a base-

\* French Patent 456,632, April 14, 1913.

† French Patent 458,033, July 27, 1912.

metal catalyst, which may be held on an inert support. The velocity of the reaction is increased by working under pressure, although extremely high pressures are not necessary. By this procedure various unsaturated organic compounds may be made to combine with hydrogen.\*

A somewhat elaborate gas-measuring system has been proposed by **deKadt**.† The amount of gas absorbed by a liquid or other material in a closed vessel, for example, in the combination of hydrogen with fats or oils in the presence of a catalyst, is determined by means of a gas meter or other measuring instrument arranged on the pipe supplying the gas and adapted to cut off the supply when a certain amount of gas has been supplied or combined. When apparatus is used in which the gas is introduced through a fine-spray nozzle at the bottom of the liquid, and unabsorbed gas from the top of the vessel is withdrawn and again introduced into the liquid, two meters are fitted upon the inlet and outlet pipes respectively so as to act differentially upon an indicator needle which thus records the difference between the volume of gas supplied and the volume unabsorbed. The needle may control an electric contact by which the gas supply is shut off and the circulating pump stopped as soon as the requisite amount of gas has been absorbed.

Fig. 34 shows the deKadt system.

The reaction vessel 1 is connected at its upper part through a suitable pipe connection 2 with a suction and force pump 3. At one part of its length this pipe connection 2 is formed into a cooling coil 4, which is located in a water reservoir 5. At the lower part of the reaction vessel 1 a nozzle or rose head 6 is provided, and from this nozzle a pipe 7 leads to the vessel 8 containing the hydrogen. This hydrogen-containing vessel communicates with the pump 3 by means of a pipe 9 and contains a cooling coil 12 provided with inlets and outlets for the supply and discharge of the cooling water.

The material to be treated, such as fats or oils, and the catalytically acting substances are supplied to the reaction vessel through a charging door 14. In the first place the hydrogen supply pipe 7 is cut off from the reaction vessel 1 and the pipe 9, connecting the hydrogen-containing vessel with the pump, is closed by a cock 15. The materials contained in the reaction vessel are then heated by means of a steam jacket or steam coil, and the air, contained in this vessel, is exhausted by means of the pump 3 and escapes to the atmosphere by way of the cock 16, the cocks 18 and 17 being open for this purpose. Hydrogen is then supplied through a pipe connected with the pump 3 and is forced into the hydrogen-containing vessel 8 through the pipe 9, the cocks 17 and 15 being open. When the necessary tension has been attained, the cocks 15 and 17 in the hydrogen supply pipe are closed and the cock 24 at the upper part of the reaction vessel connecting the vessel and pipe 2 are opened. A valve 19 is arranged in the pipe connecting the hydrogen vessel with

\* See also First Addition dated Oct. 8, 1912.

† British Patent 5773, March 7, 1912.

the lower part of the reaction vessel by opening said valve 19, behind which a reducing valve 20 is arranged; the hydrogen is conducted by the pipe 7 into the vessel 1, where it passes from the nozzle 6 through the material to be treated with which it combines to some extent, while the excess escapes upwards and is again forced into the hydrogen-containing vessel 8 by the pump 3, the cocks being suitably adjusted. The supply of hydrogen contained in the vessel, which is not supplemented by a fresh external supply during the chemical reaction, must gradually decrease in tension owing to the combination with the contents of the reaction vessel. This decrease in tension can be utilized empirically for determining the progress of the chemical reaction or for ascertaining its various stages or its completion. These indications would, however, only be approximate and deKadt therefore provides means to interrupt the supply of hydrogen to the reaction vessel automatically after the consumption of the necessary quantity of combined hydrogen.

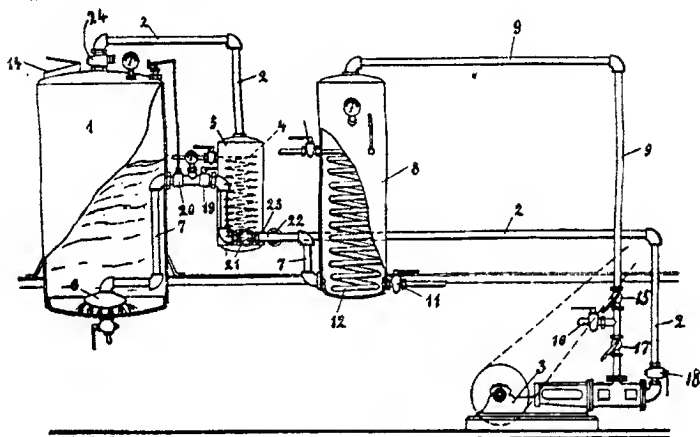


FIG. 34.

With this object a gas meter 21 is arranged on the pipe 7 supplying the hydrogen to the reaction vessel and indicates the quantity of hydrogen passing from the container 8 into the reaction vessel 1. A similar meter 22 is arranged on the return pipe 2 and measures the quantity of gas being withdrawn. Both these meters act on an indicating shaft 23 in such a manner that by the rotation of the shaft the first gas meter 21 moves the hand of indicating shaft 23 upwards, while the other gas meter 22 moves it rearwards so that the index hand shows the difference, that is to say the consumption of hydrogen. An electric contact is arranged in the path of the index hand and when it reaches a certain position, in which the necessary quantity of hydrogen has been consumed, the circuit is closed, and the hydrogen supply is cut off.

In hydrogenating oils containing the hydroxyl group, at high temperatures, this group is destroyed and **Markel** and **Crosfield** \* propose

\* British Patent 13,519, June 6, 1911.

the preparation of saturated hydroxy-fatty acids and their glycerides by treating the corresponding unsaturated acids or glycerides with hydrogen in the presence of a catalyst other than palladium and palladium hydroxide, at as low a temperature as possible, preferably just above the melting point of the final product, in order to avoid splitting off of the hydroxyl group or to control such splitting to any desired extent. Suitable catalysts recommended are iron, nickel, cobalt, copper, etc., also oxides, hydroxides and salts, which may be deposited upon suitable supports, preferably finely divided. As raw materials the mixture of unsaturated acids obtained by treatment of oleic acid with sulfuric acid, the oxidation products of linseed, cottonseed and rape oils, also castor, grape seed and whale oils may be used.

*Temperature of Hydrogenation.* For each compound there usually exists a well-defined range of temperature within which hydrogen is effectively added. Somewhere in this temperature interval lies the *mean effective temperature*, that is the temperature of maximum saturation velocity. For a number of fatty oils this approximates 180° C. or 356° F. with a nickel catalyzer. As a rule hydrogenation is accelerated more by a given temperature rise from below the mean effective temperature than the same temperature increase above this point retards the reaction. For example, raising the temperature from 170° to 180° C. increases the rate of hydrogen addition in a certain measure while elevating the temperature from 180° to 190° C. retards the rate, but to a lesser degree for such 10 degree temperature increment than the previous increase in the rate. In operation on the large scale it is, therefore, better to err by maintaining the oil slightly above rather than below the mean effective temperature, unless of course a lower temperature is prescribed because of the character of the oil. Rapidity of treatment often is desired especially in edible oils where protracted contact with the catalyzer introduces the danger of solution of the metallic material in the oil to an objectionable degree.\*

The range of temperature mentioned above varies with each type of catalyzer. Platinum and palladium, at least in certain forms, may be used at temperatures between 80° and 100° C.; nickel between 160° to 200° C.; nickel oxide and copper at about 200° C. and upwards;

\* The hydrogenation of unsaturated compounds, particularly fatty acids and their glycerides, into saturated compounds by hydrogen in the presence of finely-divided metal, according to Higgins is accelerated by the presence of formic acid or other volatile organic acid. The formic acid may be carried by the hydrogen, or the acid mixed with the material before treatment. (Chem. Abs. (1914), 437.)

all depending on the physical and chemical constitution of the catalytic material.\*

**Caro** † considers the presence of carbon monoxide in hydrogen used for hardening fats with nickel catalyzers to be, under some circumstances, injurious to the catalyzer. Maintaining the temperature of the oil during hydrogenation above 200° C. is said to be beneficial as any nickel carbonyl formed will be at once decomposed at that temperature. The hydrogenation of many substances under these conditions is not feasible and Caro recommends that the gas first be passed over nickel at 180° C. to convert the carbon monoxide into methane, which is inert.

**DeKadt** ‡ saturates fatty acids or their esters with hydrogen by the use, as a catalyzer, of a soap of a heavy or noble metal, formed from a fat or fatty acids, whose melting point lies above that of the substance to be treated.§

It is claimed by **Fuchs** || that his investigations have shown the present methods of reduction for the most part are improperly founded, causing long duration of time of treatment coupled with marked loss of hydrogen and heat; use of a great excess of hydrogen or catalyzer; injurious action of the long heating on the color, taste and odor of the reduced fat; and the application of high pressure in apparatus which involves costly autoclaves, dangerous to handle. Fuchs declares that the conduct of reduction of fatty bodies is essentially improved if the following theoretical conditions are observed:

(1) Thermal considerations: A quickening of the reaction is obtained when the oil to be treated is maintained at only a moderate temperature (0° to 150° C.), while the hydrogen employed is heated to 200° to 250° C. The avoidance of strong heating of the oil which is being treated is favorable to the quality of the final product, while preheating the hydrogen appears to increase its activity. Comparative tests show that in this way the speed of the reaction can be increased by about 10 per cent. For preheating the current of gas, copper or nickel coils in an oil bath are used. The oil bath may be

\* Ipatiew (Chem. Ztg., 1914, 374) has noted that the hydrogenation of fatty acids with metallic nickel begins at 150° C. and with nickel oxide at 230° C. The reaction progresses readily at both high and low pressures.

† Seifen. Ztg. (1913), 852.

‡ Chem. Ztg. Rep. (1913), 541, British Patent 18,310, Aug. 9, 1912.

§ **Utescher** (Seifen. Ztg. (1912), 1044) discusses from the patent point of view the claims made by DeKadt in Seifen. Ztg. (1912), 960; see also Seifen. Ztg. (1912), 900 and 1008.

|| Seifen. Ztg. (1913), 982. Reduction of unsaturated fatty acids and their glycerides, Belgium Patent 256,574, 1913.

maintained at the requisite temperature through circulation of oil heated at a distant point.

(2) Chemical considerations: Since it is impossible to have free hydrogen in its most active form, that is, in a nascent state, act upon the oil to be treated, because the quality of the oil is injured, Fuchs observes that means must be provided to apply the hydrogen in the atomic form. This can be carried out through the application of chemically active rays. Dissociation of the hydrogen molecule appears also to occur when molecular hydrogen is passed over catalytic material such as palladium black or freshly prepared nickel powder and then is allowed to diffuse under high pressure through heated plates of metal. The activity of the dissociated hydrogen, it is claimed, is from 15 to 20 per cent higher than the normal gas. The catalytic material may be placed in a tube of suitable length or on the plates of a column apparatus. By way of illustration Fuchs states that cottonseed oil carrying 0.9 per cent of a catalyzer, prepared from nickel carbonate, is raised to a temperature of 120 degrees and is subjected to hydrogen under a pressure of 18 atmospheres, the gas having been chemically activated by passage through an iron tube 3 meters in length and 60 mm. in diameter, lined with platinized asbestos and heated to 250° C. In this way by two hours' treatment a fatty body having a melting point of 44° C. was prepared. In three hours a fat melting at 65.4° C. was obtained. Fuchs notes that ordinarily from 5 to 8 hours would be required to secure such products. The claims of Fuchs' Patent call for the reduction of unsaturated fatty acids and their glycerides by means of hydrogen according to the contact process, wherein strongly heated hydrogen is caused to react on only moderately heated oil; also the treatment of oil with atomic hydrogen whose activity has been increased by treatment with chemically active rays.

The employment of nickel carbonyl by Shukoff has been described in the foregoing. In a somewhat similar manner Lessing\* makes use of a mixture of hydrogen and a gaseous metallic compound brought into contact with the substance under suitable conditions of temperature and pressure. Lessing states he has found that a great number of substances may be hydrogenated by treating them at elevated temperatures with hydrogen to which a metallic carbonyl vapor, or gas containing a metallic carbonyl, has previously been added; or with a mixture of gases, containing hydrogen in which metal carbonyl has been formed by combination of carbon monoxide, originally in the mixture, with a metal. The rapidity with which the hydrogenation

\* British Patent 18,998, 1912.



tion proceeds under these conditions may be explained as the effect of the liberation of elementary metal, the properties of which "in statu nascendi" are known to be very different from those of metal which is merely finely subdivided. Lessing observes that it has already been proposed to use as the catalyzer finely-subdivided nickel, made by decomposing nickel carbonyl in the heated material prior to the introduction of the hydrogenating gas, but it was not known that technical advantages accrue from conveying the nickel carbonyl into the material simultaneously with the hydrogenating agent so that elementary liberation of nickel occurs in close contact with hydrogen and the substance to be hydrogenated. These advantages are that the proportion of catalyzer is very much reduced and the reaction proceeds much more rapidly. Lessing carries out his process in various ways. It is convenient to introduce nickel carbonyl into the hydrogen gas by passing a mixture of the latter with carbon monoxide over reduced nickel in the well-known manner for making nickel carbonyl.

The mixture of gases employed need not be of great purity and may be made from water-gas, or by the thermal decomposition of coal gas or of coke-oven gas or of hydrocarbons of any kind, but best results are obtained when the amount of carbon monoxide in the gases is limited to that requisite for forming the nickel carbonyl necessary for the reaction, and in any case the proportion of carbon monoxide in the mixture should not exceed 25 per cent. For example, when an oil such as a glyceride or a fatty acid is being hydrogenated, the simplest mode of operating consists in passing hydrogen containing 5 to 10 per cent of carbon monoxide first through a volatilizer charged with reduced nickel and then through the oil contained in a closed vessel heated to a suitable temperature, say from 200° to 240° C. The gases passing away from the vessel are returned to the volatilizer to be used again, hydrogen or a gas rich therein being added to compensate for that absorbed by the oil. The proportion of nickel required for the hydrogenation is very small; under proper conditions excellent results can be obtained with a proportion equivalent to 0.1 part of nickel to 100 parts of oil.

Another mode of operating consists in forcing the substance to be treated, if it is in a liquid form, through spraying nozzles into a gas-tight vessel which may be suitably heated to the temperature most favorable to the catalytic hydrogenation of the substance. Into the same container, preferably at or near the bottom, hydrogen gas containing metal carbonyl, for instance nickel carbonyl, is passed. The excess of gases leaves the vessel through an outlet at the upper part and may be returned into the gas circuit after the products carried with it have been separated by condensing or washing. The treated liquid may be drained off and returned to the reaction vessel until hydrogenation has proceeded far enough. Instead of heating the reaction vessel, or in addition to doing so, the liquid may be preheated in a suitable apparatus, before entering the vessel, to a temperature required for the reaction.

By another method of carrying out the process, a solution of metal carbonyl in oil is prepared, which may be accomplished by passing the gas carrying nickel car-

bonyl through cold oil. This solution is forced through a spray nozzle into a heated vessel where it meets hydrogen whereupon hydrogenation occurs.

If the compound to be treated is in the state of gas or vapor, as for instance in the hydrogenation of the more volatile tar oils, it is simply mixed with hydrogen containing the nickel carbonyl and is subjected to the temperature required for hydrogenation. Likewise in the case of a liquid some hydrogen may be mixed with the liquid, the spray being then preferably formed by injector action instead of by liquid pressure.

The use of nickel carbonyl for the production of catalytic material also has been patented by **Kamps**,\* who introduces the carbonyl into an autoclave at a temperature above 43° C. and a pressure of 751 mm., and the oil which is to be reduced is maintained under such pressure and temperature conditions that the decomposition of the nickel carbonyl is brought about. At 60° C. the oil should be under a pressure of less than 2 atmospheres and at 180° C. less than 30 atmospheres.

Another method of utilizing nickel carbonyl for the production of catalytic material is that proposed by the **Bremen Besigheimer Olfabriken** † according to which method kieselguhr or similar porous material is saturated with nickel carbonyl and the material is heated to cause the deposition of metallic nickel on the carrier. The nickel-containing powder is immediately ground with oil to form a paste-like mass, this operation being carried out with the exclusion of air. It is also stated that the contact material may be reworked in the following manner:

It is first purified by extraction, the nickel removed and after conversion of the latter into a pulverulent form is again used for the production of nickel carbonyl. It is recommended that the carbon monoxide obtained by the Linde-Caro process in the liquefaction of water gas be used for the production of the carbonyl.

A form of apparatus adapted to be used in carrying out a process of hydrogenating oils ‡ which relates more specifically to the treatment of rancid oils or oils of high acidity is shown in Fig. 35. An oil containing a high proportion of free fatty acids or products of rancidification may be diluted with a neutral oil and the mixture hydrogenated to a hard fat, although the original rancid oil be incapable of hydrogenation, because of its poisoning action on catalyzers. The apparatus consists of a tank having a dome in which atomizers are mounted and by which the oil is atomized with hydrogen gas, and is then allowed to trickle through a series of screens placed in the lower

\* Belgium Patent 246,975.

† Zeit. f. angew. Chem. (1913), ref. 627.

‡ Ellis, U. S. Patent 1,078,136, Nov. 11, 1913.

part of the dome. Palm oil may be heated without access of air to a temperature at which its color is destroyed by hydrogenating under these conditions, producing a fat which is especially useful to soap makers.

A process for thickening oils and fats is described by **Scherieble**.<sup>\*</sup> The material to be treated is subjected to ozone-forming electric

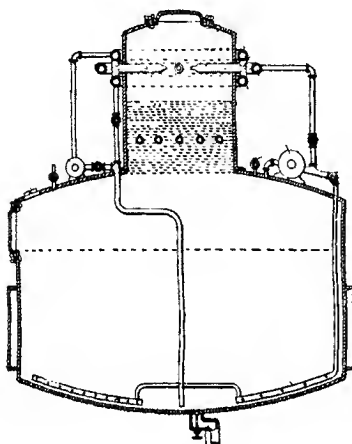


FIG. 35.

discharges by sending such discharges directly through it. Potentials of 10,000 to 20,000 volts yield no results, as oils and fats introduced between the electrodes impede any discharge by reason of their great insulating properties. Experiments in this direction have, however, shown that discharges through oils and fats are quite possible when high potentials of 50,000 to 100,000 volts and beyond are employed. The higher the potential of the electric current and the greater its frequency the easier it is to pass a discharge, with the formation of ozone, through thick layers of oil.

The oil 5 to be thickened or bleached is placed in the pan 6 (Fig. 36), the bottom of which forms one electrode, connected to the source of electricity by the conductor shown. The second electrode 8 having the terminal points 9 and fed through the conductor 10 is placed above the oil so that the discharge 11 acts upon the oily material.

By the **Calvert** system the oil is submitted to violent agitation while under a hydrogen pressure of 250 pounds per square inch and at a temperature of 180° to 200° C., in a specially constructed autoclave having an electric motor (for stirring) enclosed in a chamber which is under the same hydrogen pressure as the autoclave proper.

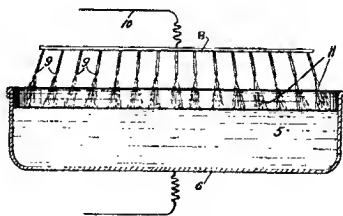


FIG. 36.

<sup>\*</sup> U. S. Patent 1,079,727, Nov. 25, 1913.

bonyl through cold oil. This solution is forced through a spray nozzle into a heated vessel where it meets hydrogen whereupon hydrogenation occurs.

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\* Belgium Patent 246,975.

† Zeit. f. angew. Chem. (1913), ref. 627.

‡ Ellis, U. S. Patent 1,078,136, Nov. 11, 1913.

An apparatus for hardening oil, proposed by **Wilbuschewitsch**,\* comprises the vessel *R* (Fig. 38) containing the fat to be treated and the vessel *O* containing the catalyst. Differentially-connected pumps *AA'* feed the oil and the catalyst into the mixing device *B* in which an intimate mixture of the oil and the catalyst is obtained. This mixture passes through a pipe *G* and the valve *H* into an autoclave *J'* which is provided with a spraying device *C'* consisting of a number of spraying nozzles so arranged that the oil and catalyst are uniformly scattered

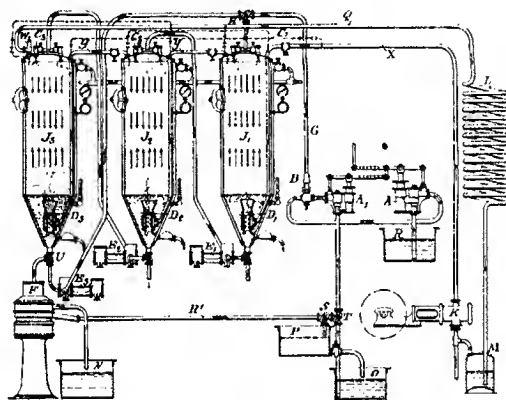


FIG. 38.

in finely-subdivided condition throughout the whole inner space of the autoclave. A compressor *K* forces hydrogen into the autoclave under a pressure of about 9 atmospheres. The pipe *X* extends from the upper part of the autoclave downward to the lower end of the same and is provided at its lower end in the conical lower part of the autoclave with an admission nozzle *D'*. By this spraying system an intimate contact of the oil mixture with the hydrogen is achieved on the counter-current principle. The autoclave is heated to between 100° to 160° C. according to the nature of the oil under treatment. The reduction by the hydrogen begins at the upper part of the autoclave. The partially reduced oil mixture collects in the conical part of the autoclave and is sprayed in the form of a fountain through the autoclave by the incoming hydrogen. The mixture is forced by pump *E'* into the second autoclave *J*<sup>2</sup>. The hydrogen enters this autoclave through pipe *Y* and the action of the first autoclave is repeated. Any

\* U. S. Patent 1,079,278, Nov. 18, 1913.

number of such autoclaves can be arranged in series or parallel to each other in accordance with the extent of reduction required. It is generally suitable to use one autoclave for each increase of melting point by  $15^{\circ}\text{C}$ . When the fat has attained the desired melting point which is ascertained by samples withdrawn from the autoclaves, the oil mixture is withdrawn through the valve *U* into the centrifugal apparatus *F*. Here the oil is separated from the catalyst. The finished reduced oil flows into the reservoir *N* while the catalyst is returned through the pipe *R'* and valves *S* and *T* to the vessels *O* and *P*. At first when the catalyst which Wilbuschewitsch employs is still quite fresh, he states that only a little of it is necessary—1 per cent may be advantageously used. When, however, in the course of the operation its catalytic power decreases, correspondingly more of it must be used. The regulation of the quantity of catalyst may be attained by a suitable adjustment of the differential pump system. When the catalyst is completely spent it is allowed to flow out through the valve *S* into the reservoir *P* in order to be regenerated. The working is continued by introduction of fresh catalyst through the valve *T*. The hydrogen not consumed passes through the check valve *W* and pipe *Q* and cooling worm *L* into a vessel *M* filled with caustic soda lye where it is purified and then passes to the compressor and autoclaves.

Wimmer and Higgins\* use as catalyzers organic metal salts such as the formates, acetates or lactates of copper, iron, nickel or cobalt. These require no special preparation before their use as catalytic agents; and it is claimed that impurities contained in the reducing gas employed in the treatment do not render these compounds ineffective. Wimmer and Higgins state that those processes in which finely-divided metals are employed in the treatment of unsaturated compounds call for the employment of intense mechanical agitation to obtain admixture of the catalysts and the liquid, or require the distribution of the metal over the outer surface of contact carriers such as pumice stone, kieselguhr, etc. By their process the compound to be reduced is mixed with the organic metallic salt, heated to a suitable temperature, and either a stream of the reducing gas is passed through the mixture, or the latter is subjected to an atmosphere of the gas in a closed vessel, while contact between the gas and the mixture or emulsion may be assisted by agitation. Under these conditions the saturation is said to take place comparatively quickly and the spent or partly spent catalytic agent can be removed by simple filtration after the operation.

\* U. S. Patent 1,081,182, Dec. 9, 1913.

According to an example given, 100 grams of cottonseed oil are mixed with 1 to 5 grams of nickel formate (in concentrated aqueous solution or in the form of a powder). The mixture is warmed and a stream of hydrogen gas passed into the apparatus. During this time the temperature of the mass is raised to from 170° to 200° C. The duration of the treatment depends upon the quantity of the catalytic agent employed. The reduction may be carried out until the unsaturated compounds are quantitatively transformed into saturated ones. The mass is then filtered.

For this process they regard the metal salts, both normal and acid, of the mono- and polybasic carboxylic acids and hydrocarboxylic acids of the fatty groups as most suitable; the formates, acetates, propionates, butyrates, lactates, glycolates, oxalates, malonates, succinates, tartrates and citrates of nickel, cobalt, iron and copper are mentioned.

"The process may be modified in various ways. Thus, for example, the oil may be emulsified with the catalytic agent and simultaneously heated and have hydrogen or gas mixtures containing hydrogen passed through it in a suitable emulsifying apparatus; or the oil mixed with the catalytic agent may be brought into contact in a fine state of division with the hydrogen, as in a manner that has already been proposed. The reaction may also be accelerated by using the hydrogen under pressure or by impregnating the oil with hydrogen and then bringing it into intimate contact with the catalytic agent."

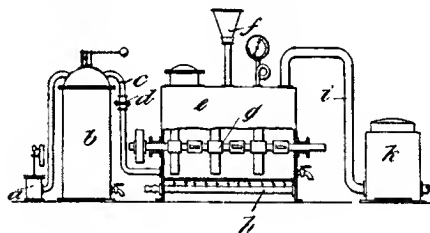


FIG. 39.

Fig. 39 is a view of an apparatus for carrying out the process. The gas is drawn by a pump *a* from a generator (not shown) and is forced by the pump into the pressure equalizer *b*. Thence the gas passes through a pipe *c*, into the receptacle *c* provided with a funnel *f* for introducing the mixture of catalyzer and oil. The mixing apparatus contains an agitator consisting of a longitudinal shaft provided with a series of revolving beaters *g*. In the base of the mixing apparatus is mounted a heater *h*. If water gas is used as the reducing agent, the portion of the gas, which has not been absorbed in the mixing apparatus, passes through a pipe *i* to a gas holder or collector *k*, and is then used for heating or power purposes.

A modified form of the inductor and tank shown in Fig. 26 is depicted in Fig. 40.\*

In Fig. 40, 1 is a treating receptacle having the inlet 2 for oil or catalyzer; a hydrogen inlet 3; a back-flash tube 4; a draw-off valve 5; a steam heating coil 6; supporting members 7; and a catalyzer inlet 8 adapted to hold capsules of catalyzer;

\* Ellis, U. S. Patent 1,084,203, Jan. 13, 1914.

11 is a pump connected with the lower part of the tank by the pipe 12 and having a discharge pipe 13 extending to an inductor 14 which is in communication by means of the inlet 15 and pipe 16 with the top of the treating receptacle 1. From the inductor the pipe 17 extends nearly to the bottom of the receptacle and terminates in a distributor 18 which is so arranged that the flow of material therethrough is both down and angularly against the bottom of the tank or receptacle.

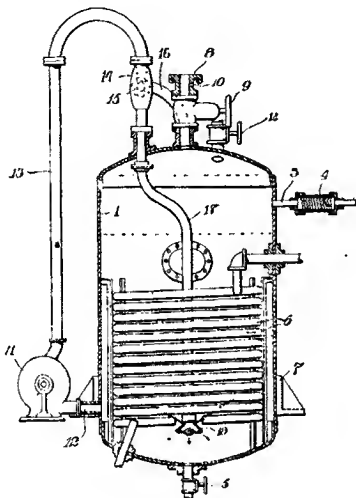


FIG. 40.

Bock\* describes several forms of apparatus intended for hardening fats and fatty acids. One of these involves passing the fatty material along or through a porous plate containing catalyzer in the presence of hydrogen. Fatty acids may be hardened under a considerable degree of hydrogen pressure and subsequently the catalyzer may be freed from the acid by distillation under reduced atmospheric pressure. Reduced nickel on kieselguhr is used as a catalyzer.†

\* Seifen. Ztg., 1914, 349.

† See also Seifen. Ztg., 1914, 421.



## CHAPTER III

### METHODS OF HYDROGENATION—Continued

IN his Inaugural Dissertation, Bedford describes a series of observations made by him prior to or during 1906 on the hydrogenation of oleic acid and certain esters of the fatty acids of linseed oil.\*

An apparatus as shown in Fig. 40a was used to bring oil, hydrogen and catalyzer into contact. The hydrogenating portion of this apparatus consisted of two communicating vertical cylinders *k'k''* partly filled with catalyzer and immersed in an oil bath. Oil was admitted to one cylinder by means of a dropping funnel while hydrogen was introduced at the bottom of the same cylinder through the glass tube shown on the right hand. The catalyzer was prepared by igniting nickel carbonate to form the oxide, forming the latter into a paste by means of distilled (chlorine-free) water and adding fragments of ignited pumice of about the size of peas. The pumice and nickel oxide paste was well stirred, the material dried at 95° and reduced in the treating apparatus by exposure to hydrogen for eight hours at 275° to 285° C. After reduction the temperature was reduced to 170° to 180° C. and the oil to be hydrogenated was allowed to fall drop by drop on the nickelized pumice while hydrogen was passed through the apparatus. Under these conditions hydrogenation took place and the treated product was duly separated from the catalyzer by extraction with ether. The nickelized pumice thus freed of oil was used again after exposure to hydrogen for one hour at a temperature of 250° C.

Bedford determined the amount of hydrogen absorbed by the unsaturated compounds examined by him in these investigations and expressed his results in part in terms of the "hydrogen number," that is, the percentage of hydrogen absorbed by the compound. When the catalyzer was used for the first time abnormal results were obtained, due, apparently, to the incomplete reduction of the nickel oxide in the preparation of the catalyzer. After using once, more concordant results were secured.

Oleic acid having an iodine number of 87.5 was treated in this apparatus and in one trial the reduction product had an iodine number of 4.1 and a melting-point of 64.5° C., while in another case the iodine number was 0 and the melting-point was 69°, indicating the complete transformation of oleic to stearic acid.

Pure oleic acid, according to theory, absorbs 0.714 per cent of hydrogen. This represents the hydrogen number of oleic acid. In two trials Bedford found

	Hydrogen Number Found.	Percentage of Theoretical Amount.
(A).....	0.7226	101.2
(B).....	0.7450	104.3

\* Über die ungesättigten Säuren des Leinöls und ihre quantitative Reduktion zu Stearinsäure, Halle, 1906.

When the ethyl ester of linolenic acid was similarly treated and the hydrogenated product (iodine number, 0) was saponified, stearic acid of melting-point  $69^{\circ}\text{C}$ . was obtained.

The hydrogen number of the ethyl ester of linolenic acid is 1.9737 and the results obtained by Bedford were as follows:

	Hydrogen Number Found.	Percentage of Theoretical Amount
(A). . . . .	1.9482	98.7
(B). . . . .	2.0408	103.4

Bedford also hydrogenated the ethyl esters of the fatty acids of linseed oil (free from oleic acid) and obtained products having numbers ranging from 24.9 to 0. The ethyl ester of stearic acid was the main product of the reaction. The hydrogen number of the ethyl ester of linolenic acid is, as stated, 1.9737, while that of linolic acid is only 1.3072. The hydrogen values found were intermediate these values.

	Hydrogen Number Found
(A). . . . .	1.4544
(B). . . . .	1.4578
(C). . . . .	1.4441

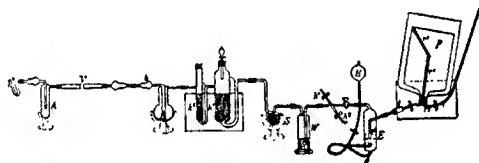


Fig. 40a.

The complete apparatus used by Bedford as shown in Fig. 40 *a* is as follows: The glass container *F* of about 18 liters capacity is used for holding and measuring the hydrogen. The mouth of the container is closed with a stopper having two perforations through which the tubes *r*<sup>1</sup> and *r*<sup>2</sup> are inserted. The receptacle is surrounded with a metal jacket holding water which enables the temperature to be maintained at the desired point. From the container *F* the tube *t* leads to an intermediate vessel *E*. *H* is a funnel containing water. *W* is a wash-bottle containing sulphuric acid. Hydrogen is introduced at *h*<sup>2</sup> and nitrogen at *h*<sup>1</sup>. *S* is a glass coil cooled by liquid air which serves for the removal of the last traces of moisture from the gases. The catalyzer as indicated above is placed in the vessels *k*<sup>1</sup> and *k*<sup>2</sup>. The vessel *B* is cooled with liquid air. A calcium chloride tube *b* is placed intermediate the latter and the tube *V*. Copper oxide is introduced into the tube *V* and in this tube the hydrogen is converted into water and the latter is condensed in the receptacle *A* by chilling with liquid air. A calcium chloride tube is also connected with the exit of the vessel *A*.

A paper by Erdmann and Bedford in *Berichte*, 1909, 1324, discusses the hardening of fatty acids and esters. Reduced nickel on pumice

was used and the oil was allowed to flow through a tower containing the catalyzer. The catalyzer is stated to be based on a modification of the method of Sabatier. Linseed oil and fatty acids were treated.

The continuous hydrogenation of unsaturated fatty acids or esters may be carried out according to the **Badische Co.\*** in the following manner: As a catalyzer is employed nickel, copper, iron, or mixtures of these metals with one another or with agents promoting the activity of the catalyzer. The process is effected under pressure of at least thirty atmospheres and preferably over fifty atmospheres, the catalyst being supported in the pressure vessel so as not to mix with the substance treated. The preparation of the catalyzer may be accomplished by reduction of an oxygen compound of the metal by means of hydrogen under pressure in the same apparatus used for the hydrogenation of the fatty acid, etc. According to examples: finely divided nickel, prepared by reduction of the oxide or carbonate at a low temperature, is supported on a carrier in the pressure vessel, or nickel pieces or wire netting is suitably held therein. Cottonseed or linseed oil is passed into the vessel and treated with hydrogen at 100° under a pressure of 120 atmospheres. Nickel carbonate or formate mixed with alumina and formed into balls or spread on a carrier, is placed on perforated trays in a cylindrical high-pressure apparatus and reduced at 220° to 250° by means of hydrogen under pressures of 30-100 atmospheres. The reduced metal is allowed to cool in hydrogen under a pressure of 30-100 atmospheres. The reduced metal is cooled in hydrogen to about 80°, and a stream of the oil to be hydrogenated and hydrogen under pressure are then introduced into the apparatus.

A laboratory apparatus for catalytic reduction is described by **Voswinckel†** which in a modified form,‡ is supplied by Bernhard To'macz & Co., Berlin. Fig. 40*b* shows the hydrogen-measuring apparatus employed.

The two thick-walled graduated cylinders *G* and *G*<sub>1</sub> are drawn out at their necks in order to do away with the rubber stoppers that were employed in the originally designed apparatus. These elongated necks are bent in the form of an L and are connected with the valves *A* and *A*<sub>1</sub> by means of pressure tubing. Of the rubber tubes *b* and *b*<sub>1</sub>, one connects the apparatus with a hydrogen tank, while the other joins the apparatus to a reaction vessel of the shaking type. The entire apparatus is mounted on a wooden frame to insure stability and render it easily transportable.

\* British Patent 2,307, Jan. 28, 1914; Chem. Abs., 1916, 125; J. S. C. I., 1915, 970.

† Chem. Ztg., 1913, 489.

‡ *Ibid.*, 1914, 634.

The two cylinders which are joined by the glass tube *D* are filled with  $1\frac{1}{2}$  liters of water. By means of air or hydrogen the water is transferred into the cylinder *G*<sub>1</sub> until the latter is full. The valve *A*<sub>1</sub> is then closed to prevent the water from flowing back in *G*. The cylinder *G*<sub>1</sub> is connected with the hydrogen tank by means of *b*<sub>1</sub> and the water is displaced by hydrogen. Valve *A* is again closed. The hydrogen tank is connected with *b*, valve *A* is opened and hydrogen is admitted until the pressure is about  $1\frac{1}{2}$  atmospheres. The cylinder *G* is then connected to the reaction chamber which has been previously evacuated. The valve *A*<sub>1</sub> is opened and the shaking machine is set in motion. When the hydrogen of the cylinder *G*<sub>1</sub> is used up, the cylinder *G*, which in the meantime has been filled with

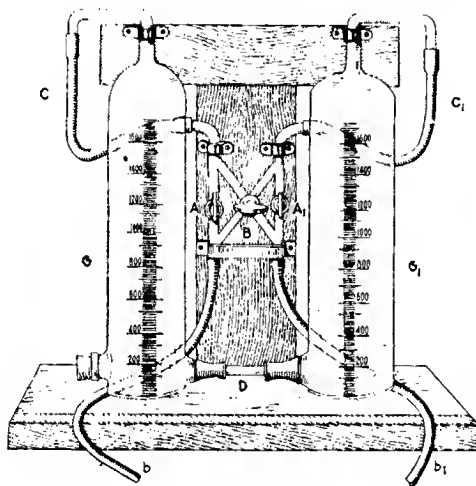


FIG. 40b.

hydrogen, is connected with the reaction chamber and *G*<sub>1</sub> is connected to the tank of hydrogen. During this operation the valves *A*, *A*<sub>1</sub>, and *B* are all shut to prevent the water from flowing back from cylinder *G*<sub>1</sub> into cylinder *G*.

Fig. 40c is an illustration of a laboratory type of hydrogenator. On the left is shown an autoclave of cast steel mounted on a tripod and equipped with a stirrer. The latter is operated by a grooved pulley and round belt which is supported on the idler shown on the right. The hydrogen gas is supplied by the pipe shown resting on the base and communicating with the autoclave through the top of the latter. A pressure gauge and safety valve are also provided. The autoclave has a rounded bottom and is surrounded by a sheet-iron mantle. It is heated by a Bunsen burner.\*

\* The autoclave was made for the author by the F. J. Stokes Company, Philadelphia, Pa.

**Dewar and Liebmann** \* seek to produce a catalyst, and to hydrogenate oil in one and the same operation and at the same relatively low temperature by mixing the fats or oils with a mixture of the oxides (either hydrated or anhydrous) or the carbonates of two or more catalytic metals, viz.: nickel, cobalt, or copper, or with a mixture of the oxides or carbonates of one or more of these catalytic metals with palladium, platinum, or silver, in a fine state of division, or with a mixture of the oxides or carbonates of one or more of these

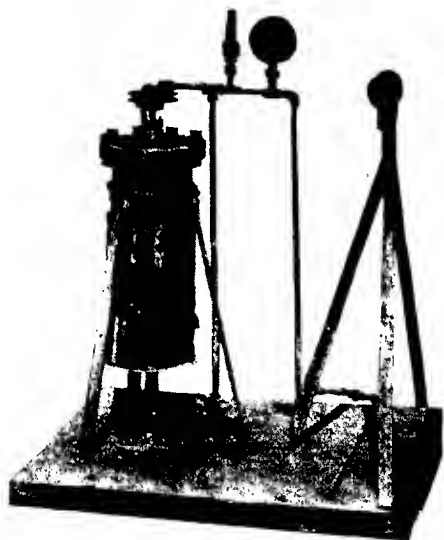


FIG. 40c.

catalytic metals with silver oxide, passing hydrogen through the mixture while it is being stirred and heating the mixture to a temperature at which the reduction takes place. Hydrogenation proceeds concurrently with the production of the catalyst and the conversion of the unsaturated body by the addition of hydrogen to the molecule is said to be very rapid.

The modifications of the process are classified by Dewar and Liebmann as follows:

A. Hydrogenation of fats and oils in a liquid state by treatment with hydrogen of an unsaturated fat or oil in the presence of mixtures of hydroxides, oxides, or carbonates of two or more of the catalytic metals, viz., nickel, cobalt, or copper.

\* J. S. C. I., 1915, 797; British Patent 12,982 of 1913; Mat. grasses 1915, 8, 4377; Chem. Abs., 1916, 284.

*B.* Hydrogenation of fats and oils in a liquid state by treatment with hydrogen of an unsaturated fat or oil in the presence of a mixture of one or more of the metallic compounds as defined in *A* with finely-divided palladium, platinum, or silver.

*C.* Hydrogenation of fats and oils in a liquid state by treatment with hydrogen of an unsaturated fat or oil in the presence of a mixture of a metallic compound as defined in *A* and silver oxide.

*D.* Hydrogenation of fats and oils in a liquid state by treatment with hydrogen of an unsaturated fat or oil in the presence of the mixtures mentioned in *A*, *B* and *C*, produced on the surfaces of porous substances.

The following examples will serve to illustrate the process:

1. A solution of 89.2 parts by weight of nickel nitrate (crystals) and of 9.3 parts of copper nitrate (crystals) is poured into a hot solution containing 46 parts of potassium carbonate. The precipitate is collected on a filter, washed thoroughly until free from soluble salts and then dried on the water-bath; it is then heated to a temperature below red heat until the weight is constant. One hundred parts of cottonseed oil are then stirred with a quantity of the oxide thus prepared, the metal contents of which correspond to two per cent of the weight of the oil. A strong current of hydrogen is passed through the mixture which is heated for two hours at about 190° C. while being continuously stirred. On cooling, the oil is found to be hard and very nearly saturated, the iodine number being reduced from 110.6 of the original oil to 20.4.

A similar experiment carried out with the same mixture of oxides and whale oil shows after an hour reduction of the iodine value from 114.8 to 20.6 and after two hours to 1.9.

2. One hundred parts of whale oil are mixed with a quantity of nickel and copper hydrates (containing 90 per cent of metallic nickel and 10 per cent of copper) in proportion of about 2 per cent of the metals to the weight of the oil and a strong current of hydrogen is passed through the mixture while it is being continuously stirred and heated for one hour at about 185° C. The iodine value of the whale oil is thus reduced from 128.8 to 32.3 and the oil is quite hard.

3. Nickel and copper carbonates are prepared in molecular proportions in the manner described in No. 1, and a quantity of the carbonate, the metal contents of which amount to about 2 per cent of the weight of the oil used, is mixed with cottonseed oil and a strong current of hydrogen is passed through the mixture, while it is being continuously stirred and heated for two hours to about 185°. The iodine value is reduced from 113 to 38.6.

4. 44.6 parts of nickel nitrate (crystals) and 2 parts of palladium chloride are dissolved in water with the addition of a little hydrochloric acid. The solution is warmed and added to a hot aqueous solution containing 15 parts of caustic soda and 2 parts by volume of 40 per cent formalin. A dark gray precipitate is obtained, collected on a filter and dried on the water-bath.

One hundred parts of whale oil are mixed in an autoclave with 3 parts of the product thus prepared (about 2 per cent of metal contents) the autoclave closed and the mixture being well stirred and heated (while hydrogen is passed through) to about 180° or 190°, the outlet of the hydrogen being so regulated that the pressure in the autoclave is about 140 lb. After half an hour the oil, on cooling, is quite hard, the iodine number being reduced from 128.8 to 36.1.

5. Whale oil is mixed with nickel hydrate and silver oxide (90 per cent nickel and 10 per cent silver) in proportion of about 2 per cent of the combined metals

to the weight of the oil used. A strong current of the hydrogen is passed through the mixture for two hours while it is being continuously stirred and heated up to about 195°. The iodine value of the oil is reduced from 114.8 to 62.1.

6. Asbestos is impregnated with a solution containing equal parts of nickel nitrate (crystals) and copper nitrate (crystals) in such strength that the metal contents of asbestos and oxides, after their production, amount to 20 per cent of the combined weight of metal and carrier. The impregnated asbestos is dried and heated to convert the nitrates into oxides. Seventy-five parts of cottonseed oil are mixed in an autoclave with 5.5 parts of the asbestos thus prepared (the metal contents amounting to about 1 per cent of the oil) the autoclave is closed and the mixture heated while being well stirred and hydrogen is passed through it at about 180° to 190°. The outlet of the hydrogen is so regulated that the pressure in the autoclave is about 140 lb. After half an hour the oil on cooling is quite hard and practically converted into a saturated compound, the iodine value being reduced from 113 to 2.7.\*

Dewar and Liebmann treat fats and oils with hydrogen† in the presence of a catalyst distributed over a mass of fibrous and coherent material or yarns or fabrics made therefrom, and arranged so that fibers will not become separated from one another. With this arrangement the tedious operation of filtration is avoided.

The fibrous material may consist of cotton, hemp, flax, or jute, wool, silk, or similar natural organic fibrous materials, or even artificial silk, e. g., viscose silk freed from sulphur. Sponge also may be used. Separation of the fibers is prevented by enclosing the masses between screens of gauze or other suitable material, or by securing with wires or threads; or if yarns or fabrics are used, these may be wound round or otherwise secured to the blades of an agitator or to fixed supports. If strongly adherent masses of fibrous materials, such as cotton, silk or flax, or yarns or fabrics made therefrom, be used, the masses may be left free to move in the liquid, but the products of hydrogenation are not so satisfactory. If nickel, cobalt, or copper is used as the catalyst, the oxide or carbonate of the metal is distributed on the support, and the catalyst produced before or during the process of hydrogenation. In the case of the platinum group of metals, the catalyst is prepared by impregnating the materials with a platinum or like salt solution and then treating with a hot alkaline solution of formaldehyde. In examples, cotton or linen yarn, or bleached artificial silk yarn freed from sulphur or asbestos cord is passed through a solution of nickel and copper compound, and after squeezing, treated with soda solution and dried. The material is wound on a nickel gauze cylinder or on the blades of the agitator, and placed in an autoclave with the oil. In another example, silk yarn, on which nickel and copper carbonates were distributed as in the previous example, is wound on the plates of an agitator and washed, first with water and then with nickel acetate solution and finally with water ‡

\* See Canadian Patent, Procter & Gamble Co., 178,021, July 3, 1917; Chem. Abs. 12, 98.

† British Patent 15,668, June 30, 1914; J. S. C. I., 1915, 1102; Chem. Abs. 1916, 125.

‡ U. S. Patent, 1,222,608, Aug. 17, 1917. Canadian Patent, Procter & Gamble Co., 178,020, July 3, 1917.

A process of, and apparatus for, making lard substitute is proposed by Chisholm.\*

In Fig. 40*d*, a casing, mounted upon supports, is provided at the top with a pressure gauge and a gas outlet which may be set to discharge the gas at any desired pressure. Centrally and rotatably mounted within the chamber is a catalyzing element, consisting of a spool-like support wound with wire formed of or coated with a catalytic agent, the wound mass being sufficiently porous

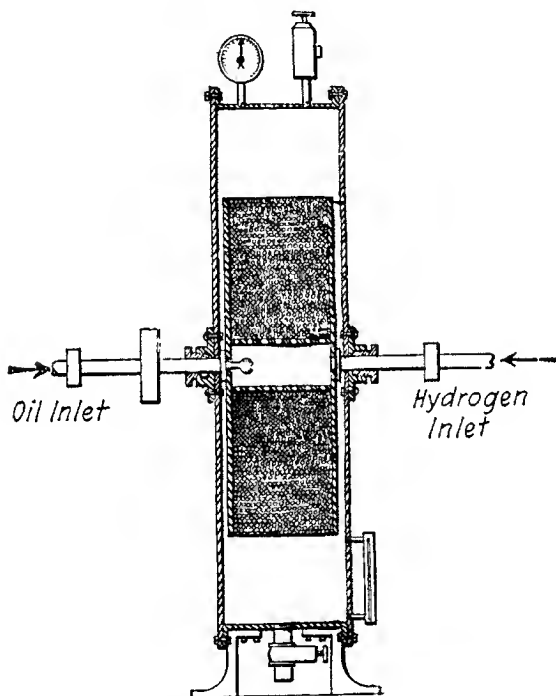


Fig. 40*d*.

to permit of the passage of liquid and gas outwardly thereof, the liquid and gas tending to follow the spiral course of the wire in its passage outward. In the construction of the catalyzing element, No. 20 copper wire with a rough black, unpolished electrolytic deposit of nickel thereon is used. Wire of nickel or palladium which has been roughened also may be employed. Within the spirally wound mass of wire is a central chamber with which there is rigidly connected an inlet pipe to provide hydrogen gas. A pipe on the opposite side

\*U. S. Patents Nos. 1,113,151, Oct. 6, 1914; 1,114,963, Oct. 27, 1914; J. S. C. I., 1914, 1062, 1108; Chem. Abs., 1914, 3828; 1915, 110.



supplies oil to the apparatus. The pipes are rotatably mounted within bearings secured upon opposite sides of the casing and the oil pipe is provided with a driving pulley. A satisfactory size for the casing is 3 ft. 6 in. in diameter and 6 in. thick with inlets at opposite sides of  $\frac{1}{2}$  in. The catalytic agent may have a diameter of 23 in. and a thickness of  $5\frac{1}{4}$  in., the inner chamber being approximately 3 in. in diameter. On being revolved, the catalyzing element moves the oil and gas outwardly along the lines of the spirally-wound wire. A temperature of  $160^{\circ}$  is employed. The hydrogen and oil may be introduced under pressure. The lard-like fat resulting from the treatment of cottonseed oil in this manner is collected in the lower part of the casing.

**Kimura** \* agitates an unsaturated fatty oil, a catalyst such as nickel carbonate and hydrogen gas in a vertical cylinder enclosed in a steam jacket.

A central vertical shaft carries an agitator comprising a framework, star-shaped in horizontal cross-section, each radial portion being covered by metallic netting of nickel, platinum, iron, or silver. The central shaft also carries a supporting spider for the spindles of similar planet agitators which thus revolve around the central agitator. Each planet spindle carries a spur-wheel which engages with an internally toothed ring on the wall of the container. The central agitator causes a centrifugal movement of the liquid outwards, and the rotation of the planet agitators causes an intimate mixing and subdivision.

An endeavor has been made by **Rather** and **Reid** † to determine the nature of the reaction between ethylene and hydrogen from the quantitative standpoint. The method employed for bringing about reaction differs from that of Sabatier and Senderens of passing a mixture of gas or vapor and hydrogen over reduced nickel in a long tube. The method of Rather and Reid to a certain extent is a sort of combination of the Sabatier and Senderens method and the present method of hydrogenating non-volatile oils by agitating with a catalyst while bringing hydrogen into contact with the oil.

Details of the experimental work carried out by Rather and Reid are given below:

**Preparation of the Catalyst.** One hundred grams of infusorial earth were treated with a solution of 50 g. nickel nitrate,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , in about 150 cc. water, and the resulting moist mass added to a strong water solution of 60 g. sodium carbonate,  $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ , to precipitate the nickel as carbonate. The product was well washed and dried and the nickel carbonate reduced by heating, in a glass tube, just below red heat, in a current of pure dry hydrogen till no more water was formed, and cooled in a current of pure dry carbon dioxide. In order to standardize the catalyst, its activity was tried with cottonseed oil, 70 g. of the oil and 1 g. of the catalyst being treated with pure dry hydrogen at  $180^{\circ}$  in the apparatus described on p. 76. The iodine number of the oil was lowered, in

\* British Pat. 113,232, Aug. 31, 1917; J. S. C. I., 1918, 187.

† J. Am. Chem. Soc., 1915, 2115.

sixty minutes' treatment, from 113.7 to 41.6. Experiment showed that the catalyst did not deteriorate appreciably during the time that each portion of it was in use.

**Temperature.** In all of the experiments, the temperature was maintained at  $180^{\circ} \pm 1^{\circ}$  by immersing the bulb of the reaction-flask in an oil-bath, the temperature of which was maintained constant by an oil thermostat with mercury contacts, controlling a gas regulator.

**Materials.** The ethylene was made according to method of Senderens and washed with sodium hydroxide solution. The hydrogen was from zinc and acid and was washed with alkaline potassium permanganate. As an inert medium, in which to suspend the catalyst, melted paraffine was used.

**Procedure.** The gas mixtures were prepared in gasometers, holding about 24 l., which were provided with an arrangement for maintaining nearly constant pressure. The same lot of the mixture was used for the whole series of experiments on any one proportion. Each mixture was analyzed for ethylene by the usual method with fuming sulphuric acid. The mixture of gases was run through concentrated sulphuric acid to dry it and then into the reaction flask which contained, in each experiment, 1 g. of the catalyst, and 70 g. of the paraffine. The stirrer was run at 3300 to 3500 r.p.m. In each case, time was allowed for the displacement of air from the apparatus and for the hot paraffine to come to equilibrium with the ethylene, hydrogen, and ethane passing through it. The attainment of this equilibrium was shown by constancy in the analysis of the successive samples of the issuing gases. The amount of ethane in the product, which is the same as the percentage of reduction of the ethylene, was calculated by the following formula, in which  $E_1$  is the percentage of ethylene in the original mixture and  $E_2$  is the percentage of ethylene in the products of the reaction.

$$\text{Ethane} = - \frac{100E_1 - 100E_2}{100 - E_2}$$

Fresh lots of catalyst and paraffine were used for each 24 l. of mixture. The rate of gas flow and the composition of the original mixture are the only variables studied.

The results are by no means as regular as could be wished, and some are evidently out of relation to the others. They are not to be considered as final. The irregularities may depend on factors not as yet known or controlled. In Fig. 40c the percentage of the ethylene reduced is plotted against the rate of flow. The interesting result is that, for all of the mixtures, about 70 per cent of the ethylene is reduced when the rate of flow is 10 cc. per minute. All of the results for the 10 per cent mixture are regular and as would be expected. Those for mixtures containing higher percentages of ethylene are by no means so regular and the curves are in unexpected relations to each other. Doubtless the determining factor is solubility. The reaction is probably taking place between the ethylene and the hydrogen that are dissolved in the paraffine. The mass law then holds for this solution and not for the gases that are not in solution. When the passage of the gas mixture is rapid, the gases are swept through before equilibrium can be established between the gas mixture and the solution.

In Fig. 40f the volume, in cc., of gases made to combine, per minute, is plotted against the rate of flow. As was to be expected, this amount increases with the amount of the gas mixture that is exposed to the action of the catalyst. The results

for the different mixtures are in the expected order, those for the rate of 100 cc. per minute being the most instructive. Under these circumstances, in the 50 per cent mixture, 17 cc. of hydrogen is made to combine with 17 cc. of ethylene in one minute. Since the 1 g. of the catalyst, as prepared, cannot contain more than 0.1 g. nickel, the volume of this, considered as Ni, would be about 0.01 cc. or less. Hence the catalyst induces the reaction in 3400 times its own volume of the gas mixture in one minute. In the experiment with cottonseed oil, given above, the same amount of nickel caused the absorption of 4230 cc. of hydrogen or 423,000 times its own volume of hydrogen in sixty minutes, or 7000 times its own volume in each minute. These volumes are calculated for a temperature of 0° and would be 67 per cent greater at 180°, at which the action really took place. The amount of hydrogen caused to combine with the oil is several times as great as the amount

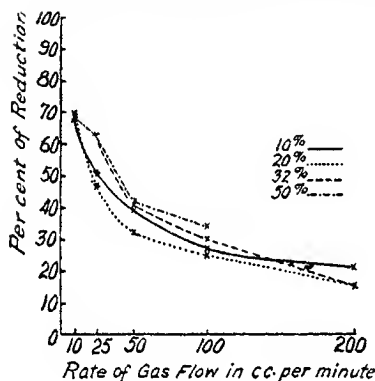


FIG. 40e.

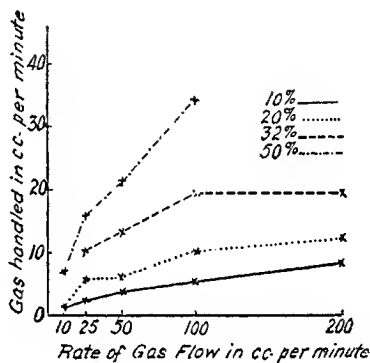


FIG. 40f.

combined with the ethylene, which is as would be anticipated, as the concentration of the ethylene in the paraffine is probably much smaller than the concentration of the olefine in the oil, and the partial pressure of the hydrogen in the mixture is only half so great as in the pure hydrogen. However, the results are of the same order of magnitude.

In the process of **Asp Bock** (see p. 49) of treating fats with hydrogen a porous metal in the form of plates or blocks, is used as a catalyzer. Either the hydrogen and fatty acids are allowed to pass in vapor form through the porous metal, or the oil is passed through the porous metal at the ordinary temperature and pressure while the hydrogen rises through the pores. These methods may be combined. The first method is preferred for fatty acids, the other for glycerides.\*

A hydrogenation process employing hydrogen under pressure is proposed by **David**,† according to which gas is forced into the lower

\* Chem. Abs., 1915, 868; Danish Patent 18,332, March 27, 1913.

† J. S. C. I., 1915, 186; French Patent 470,392, June 14, 1913.

part of the first of a series of connected cylinders containing the mixture of melted fat and catalytic agent. The fat is intermittently projected upwards and falls from depending plates, preferably of nickel, into the current of gas, while a hot-air jacket maintains the temperature at 150° to 200° C. The hydrogen passes through several of the cylinders before being returned to the gas holder to be purified, compressed, and used again.

**Adam**\* secures intimate contact between the reacting materials in the catalytic hydrogenation of liquids, by bubbling the gas from a number of points into a body of liquid, coalescence of gas bubbles from adjacent delivery points being prevented by suitable partitions.

A form of Adam's apparatus is shown in Fig. 40g.

In this apparatus a tall vessel *a* is provided with an assemblage of tubes *b*, supported by the supports *c*. These tubes are set closely together and are open at both ends. They may be of any desired cross-sectional form, and although shown straight may be somewhat spiralled where increased contact is desired. Beneath the tubes and at a little distance away is a gas manifold *d* connected to the gas supply duct *e* leading from the upper part of the vessel *f*, to the blower *h*. From the gas manifold nozzles *k* project in to the tubes *b*. Gas is introduced at *g*.

By appropriate choice of the relative diameter and height of the tubes, the number of nozzles to each tube, and adjustment of the gas flow, and of the height of the liquid supplied to the tubes the character of the contact can be varied from that of a climbing film to that of a tall column of froth.

The heating of the material can conveniently be effected by electric heaters immersed therein, and these may be formed, for instance, by insulating the tubes from each other at the top and bottom, and so converting them into a series of heating elements.

In the **Grüner** process of bleaching and thickening oils and fats† electric currents are passed through the material in an acid atmosphere, the tension and frequency of the discharges being such that the mass is kept in vigorous motion.

Röntgen rays have been suggested as an aid in hydrogenating fats. **Wielgolaski**‡ brings hydrogen into contact in various ways with fats or fatty acids while exposing the material to Röntgen rays.

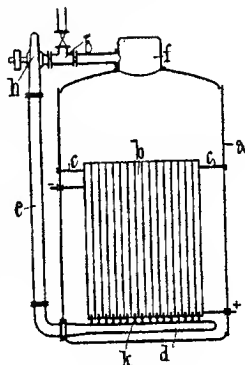


FIG. 40g.

\* J. S. C. I., 1914, 1226; British Patent 24,815, Oct. 31, 1913.

† Holland Patent 1,142, Feb. 4, 1916; Chem. Abs., 1916, 1715.

‡ Seifen Ztg., 1914, 1195; Norwegian Patent 24,528, 1913.

In one case \* oils are passed through electrodes which have a porous filter-like form and are subjected to electrical action.†

Experiments were performed by Custis ‡ to ascertain if there would be an acceleration of the hydrogenation of oleic acid under the influence of the rays from an iron arc. The hydrogen was led into a quartz flask, which contained the oleic acid. A long air condenser was passed through the stopper with which the flask was supplied. An iron arc was placed 1.5 centimetres from the flask, and exposure was allowed to proceed for six hours. From the iodine numbers of the acid before and after treatment the conclusion was reached that there is no acceleration in the hydrogenation of oleic acid when hydrogen acts on the acid in the presence of rays from an iron arc under ordinary conditions of temperature and pressure. Blank experiments showed an amount of saturation equivalent to that found in the exposed fatty acid.

Charlton,§ has devised apparatus by which saturation is effected in a closed rotating drum provided on its inner periphery with blades which break up the oil and bring it into intimate contact with hydrogen. The gas is introduced under pressure through a flexible tube and a reducing valve from a cylinder attached to the drum and moving with it. Steam is admitted to an outer casing of the drum through a passage in one of the trunnions and escapes through the other trunnion. The drum is preferably made to rotate nearly a complete revolution alternately in opposite directions.

An apparatus is described by Verona Rinati || for the hydrogenation of oils, in which palladium precipitated on small pieces of coke is used as a catalyst.

The catalytic material is placed on a movable support kept in motion by a rotating spindle connected by gearing with a pulley outside the reaction chamber. Oil which has previously been heated is sprayed into the upper part of the chamber by means of hydrogen under pressure, and a pressure of about two atmospheres is maintained inside the chamber. Three reaction chambers are provided and the oil may be withdrawn after one, two, or three treatments, according to the degree of hydrogenation desired. The hydrogen is obtained from water-gas by the Frank-Linde-Caro process of refrigeration, and all the excess coming from the reaction chambers is returned to the refrigerating apparatus for purification. When the catalyst loses its activity, it is washed in the apparatus with an inert solvent (benzine), the last traces of the latter are expelled by a current of steam, and the palladium is again rendered active by

\* Norwegian Patent No. 25,000.

† A full description is given in *Seifen Ztg.*, 1915, 73.

‡ *J. Frank. Inst.*, 1917, 880.

§ *J. S. C. I.*, 1915, 289; British Patent 1,410, Jan. 19, 1914.

|| *Annali Chim. Appl.*, 1914, 2, 99-105; *J. S. C. I.*, 1914, 1061, *Chem. Abs.*, 1914, 3723.

reatment with hydrogen at not above 150° C. Palladium possesses the advantage of being active at a considerably lower temperature than nickel (e.g., at 0° to 90° C.).

At the Vereinigte Chem. Werke at Charlottenberg, according to Solletas \* hydrogenation of oils is effected at 100° C., under a pressure of 2 to 3 atmospheres by means of 0.00002 part of palladium chloride in the presence of an alkali. The loss of catalytic agent is from 5 to 7 per cent of the weight taken, which corresponds to an expense of 1.60 francs per 100 kilos of fat.

A simple and effective method of treating oils containing finely-divided catalyzer with hydrogen is described by the author † accord-

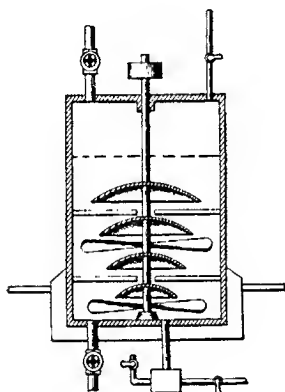


Fig. 40h.

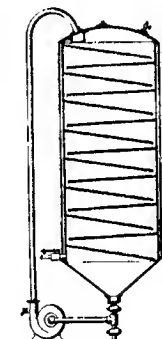


Fig. 40i.

ing to which the oil and catalyzer is exposed to an ascending current of the gas. The oil and catalyzer mixture is caused to circulate in a direction approximately transverse to the direction of flow of the stream of hydrogen.

Apparatus for the purpose is shown in Fig. 40h. A treating tank is equipped with a shaft, carrying mixing blades. Hydrogen is entered by a pipe at the bottom and passes out of the apparatus by an exit pipe at the top. The bell-shaped affairs on the shaft may be used for the purpose of intercepting the downward flow of the gas, permitting of a longer period of contact. The tank is filled with oil containing catalyzer, finely-divided nickel from nickel carbonyl being suitable for this purpose. The stirring apparatus is put in motion and hydrogen introduced. The oil hardens very satisfactorily by this treatment.

\* Les Matières Grasses, 1914, 7, 4151; J. S. C. I., 1914, 972.

† U. S. Patent 1,095,144, April 28, 1914.

**Humphreys** \* hydrogenates oil with an apparatus consisting of a closed chamber (Fig. 40i) having within it slightly inclined, supporting plates, one above the other, and successively discharging at their lower edges onto the upper portions of the next succeeding plate with means at the bottom of the chamber for collecting the material being acted upon and delivering to a pump which conveys it back to the top of the chamber to complete the path of circulation.

**Mandelstam** † hardens oil by a combined spraying and lubbering method employing apparatus as shown in Fig. 40j. A closed tank heated by a steam coil is two-thirds filled with oil carrying a catalyzer in suspension. The pumps shown on either side of the tank withdraw the oil and catalyzer mixture from the lower part and spray it into the gas space in the upper part of the tank.

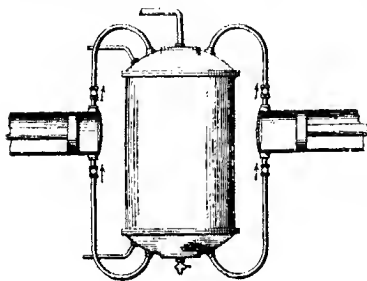


FIG. 40j.

Hydrogen is admitted by the pipe shown in the middle of the top of the apparatus and is forced into the oil at various places in the tank by means of sprayers or distributing devices.

An interesting system of hydrogenating oils is described by **Moore**.‡ The oil is fed in a continuous stream into the upper portion of a closed chamber, where it meets a blast of hydrogen and is atomized. The chamber is provided with a pervious filtering diaphragm containing a catalyzer, and the mixture of oil and hydrogen in excess penetrates the diaphragm into contact with the catalyzer whereupon the oil is saturated, and the hydrogenated oil and the excess of hydrogen pass into the lower portion of the chamber.

The excess hydrogen may then be freed of oil and re-used, and the hydrogenated product withdrawn in a continuous stream. To secure the greatest possible active surface, the catalyzer consists of a layer of finely-divided or pulverulent material confined between layers of filtering material. It is stated to be difficult to force a large body of oil through such powdery mass, but, when the oil is atomized, it may be forced therethrough without difficulty if the pressure be sufficient.

Moore finds that proper results cannot be obtained after the particles of the

\* U. S. Patent No. 1,100,735, June 23, 1914.

† J. S. C. I., 1914, 1162; U. S. Patent 1,114,623, October, 20, 1914

‡ U. S. Patent No. 1,121,860, December 22, 1914; 1,184,480, May 23, 1916; J. S. C. I., 1915, 144. Canadian Patent 172,839, Oct. 31, 1916.

catalyzer become covered with films of oil, for the reason that the hydrogen is unable to obtain access thereto, and hence he provides for cleaning the catalyzer of the oil and thereby revivifying the former. This is accomplished by causing the constant passage of hydrogen through the catalyzer, and also by arranging the nozzles for the oil and hydrogen in such manner and so moving them that the spray is directed progressively toward restricted areas of the mass of catalyzer. Hence, through that portion of the catalyzer which at the moment is not receiving the spray, hydrogen is passing through in such quantities and at such velocity as to blow off or remove the films or coatings of oil which

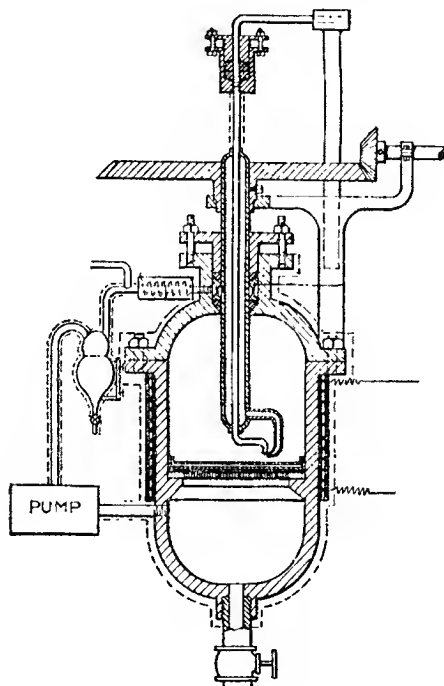


FIG. 40k.

enclose the particles. Thus each restricted portion of the catalyzer first receives the mixture of oil and hydrogen, and is then freed of the oil, either as such or in saturated or partially saturated condition. By this procedure the quantity of oil which any one portion of the diaphragm and the catalyzer is receiving is relatively small, and the oil is so broken up and mixed with the hydrogen that it is readily carried through the catalyzer bed, and hydrogenated instantaneously, so it is claimed. By regulating the oil supply, the degree of solidity of the hydrogenated product is adjusted to any predetermined point, according to the use for which it is intended.



In Fig. 40*k*, an apparatus is shown consisting of a cast-metal casing forming a cylindrical chamber, transversely divided by a filter diaphragm containing the catalyzer. The diaphragm consists of a perforated plate, upon which rests a layer of wire cloth, preferably about 100 mesh. Upon the wire cloth is a thin layer of suitable inert material, such as a mat of asbestos fiber. Upon the layer of asbestos is a thin layer of the catalyzer, and upon this is placed another layer of asbestos. The oil and hydrogen are introduced into the upper compartment through down-turned nozzles. These nozzles are so located that the blast of hydrogen, traveling at high velocity, impinges upon the stream of oil flowing from the nozzle and atomizes the latter, directing the spray across the surface of the diaphragm. The nozzles revolve and thus direct the spray progressively in a circle over the entire surface of the diaphragm.

The Moore process of hydrogenation used at the plant of the Berlin Mills Company, Berlin, N. H., is discussed by **Hendricks**,\* who states that the plant is of a very highly developed semi-commercial nature with a capacity of 30,000 pounds daily.

The **Ney** process of hydrogenation is carried out with the apparatus in Fig. 40*l*.

In describing his process Ney observes that the generally accepted theory for the explanation of catalytic reactions is the formation of certain instable intermediate compounds of the catalyst with one or more of the reagents. In the instance of the catalysts, like nickel, the formation and decomposition alternate of a nickel-hydrogen compound or hydride is hypothetically presumed. It is

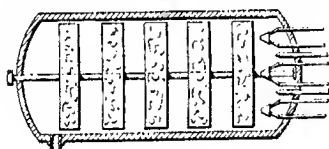


FIG. 40*l*.

immaterial for the purpose of the present consideration whether these hydrides are stable for any length of time under certain conditions or whether they always instantaneously are formed, decompose and are re-formed. In the technical application of catalytic reduction the fact alone is of importance that under certain favorable conditions the formation of the hydride takes place and subsequently an exchange or transfer of the hydrogen atom from the hydride to the organic body. In considering the dynamics of this reaction it is apparent that the hydrogenation of organic bodies must take place in a series of distinct phases. When the organic body first comes in contact with prepared catalyst in the presence of hydrogen, an instantaneous transfer of the stock of hydrogen already present in the catalyst takes place. Subsequently if the catalyst is again exposed to the influence of a fresh supply of hydrogen, a reformation or regeneration of hydride follows, followed by a renewed transfer of hydrogen to fresh material until all unsaturated bodies have become saturated ones. It is, however, clear that this is only the case if the catalyzer is permanently kept free of the organic material or where the organic body can be maintained in form of a true vapor or gas under the conditions of hydrogenation.

In case of organic material incapable of being transformed into the vaporous

\* J. Ind. Eng. Chem., 9, 795.

to gaseous state, entirely different conditions prevail. When the material, such as a mixture of the glycerides, of unsaturated fatty acids meet first the catalyzer, the first of the above mentioned phases takes place. However, as the hydrogenated material and the excess of the original product keep on flowing over the catalyzer or reaching it in some other way, these bodies are not immediately removed as in case of a true vapor or gas but rather on account of certain physical properties as viscosity, surface adhesion and capillary energy, adhere strongly and tenaciously to the catalyst or its carrier, thus preventing or greatly impeding the reformation of the hydride due to the sealing up of the surfaces of the catalyst and preventing the access of the hydrogen to it.

In Ney's process catalyzer is placed in baskets mounted on a shaft arranged to rotate in a chamber containing hydrogen. Oil is atomized in the chamber by means of the atomizers shown on the right of the illustration, and the "oil-fog" produced impinges on the catalyzer. Owing to the relatively slight centrifugal force exerted upon the oil-fog, its penetrative properties are inherently good, while as coagulation of the oil occurs so that a concrete drop or particle is produced, then centrifugal action manifests itself and the concrete oil particle is ejected from the basket or drum. Hence it follows that while the catalyzer is freely in contact with the fog particles in the presence of the hydrogen gas, the discrete or concrete particles of oil are removed from its surfaces by centrifugal action, and thereby the catalyzer is revived or prevented from becoming sealed away from the hydrogen gas, and its action upon the oil is constant and effective. Thus, the reformation of the hydride (or other action produced by the contact of the catalyzer and hydrogen), is continually in progress. A catalyzer of substantially constant hydrogen (or hydride) content is secured.\*

In Maryott's process † fats or fatty acids are dissolved in some fat solvent, such as alcohol, acetone, ether, petroleum ether, benzene, chloroform, carbon disulphide, carbon tetrachloride, or other fat solvent and the fat or fatty acid, while in the solvent, is subjected to the action of hydrogen in the presence of some catalyzer, preferably palladium.

It is not necessary that the fatty substance be completely dissolved in the solvent, for triolein, for instance, in alcohol at a temperature below that at which it is completely soluble, is readily reduced in the presence of finely-divided palladium. In general, a solution containing about 25 to 50 per cent of fat is preferable.

The process can be carried out in a reaction chamber provided with an agitator and suitable means for regulating the temperature and gas pressure. The solution of the fat or fatty acid in the fat solvent containing in suspension the catalyzer, preferably deposited on some finely-divided material as asbestos, is introduced into the chamber, and kept agitated to insure a uniform mixing with the catalyzer, while the temperature is suitably regulated, and the hydrogen conducted into the chamber under appropriate pressure. While the unsaturated fatty bodies, when dissolved, for instance, in alcohol or acetone, are

\* U. S. Patent No. 1,185,704, June 6, 1916.

† U. S. Patent No. 1,097,456, May 19, 1914.

hydrogenized in the presence of finely-divided palladium at room temperature under atmospheric pressure, a higher temperature and a greater pressure favor the reduction. After the reduction has proceeded sufficiently far, as shown by tests of samples withdrawn, the mixture is removed from the reaction chamber, the catalyst separated by filtration, and the solvent distilled off either at atmospheric pressure or at reduced pressure, or without distilling off the solvent the reduced fatty substance may be largely removed by cooling and filtering off the separated fat.

Instead of agitating the solution of the fat or fatty acid in the reaction chamber, the solution containing the suspended catalyst can be sprayed by means of an atomizer into a chamber of hydrogen, and after sufficient action the mixture can be treated as above for the removal of the catalyst and the solvent.

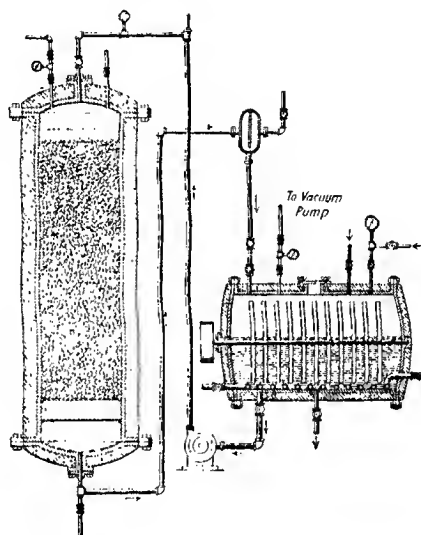


FIG. 40m.

The influence of the solvent in facilitating the action of the hydrogen on the fat or fatty acid in solution might find an explanation according to Maryott, in the better opportunity afforded for the freer diffusion of the reacting substances. Maryott states that benzene, gasoline, and ether are solvents which greatly increase the speed of the reaction.

According to the **de Jahn** process,\* oil is agitated with hydrogen in one vessel and then passed through a second vessel containing the catalyst. The circulation of the fat is continued until hydrogenation is complete. The apparatus used by de Jahn is shown in Fig. 40m,

\* U. S. Patent No. 1,131,339, March 9, 1915; J. S. C. I., 1915, 434.

the agitating vessel appearing on the right, and the catalyzer chamber on the left of the illustration.

The catalyzer, which may consist of cobalt, palladium, or nickel, is carried in thin layers on an inert material, such as porous burnt clay lumps or pumice stone.

Various forms of apparatus are employed by Calvert,\* one of which is shown in Fig. 40*n*, and consists of a gas-tight inclosure comprising a commingling chamber *a*, a motor chamber *e*, and a pipe *d* connecting the two. The liquid to be treated such as oil, is placed in the commingling chamber *a*. The commingling means is in the form of stirrer blades *c* mounted on a shaft *b*, which passes through the pipe *d* and is driven by a motor *f* located within the motor chamber *e*. In the case of the hydrogenation of oils *f* is preferably a motor of the induction

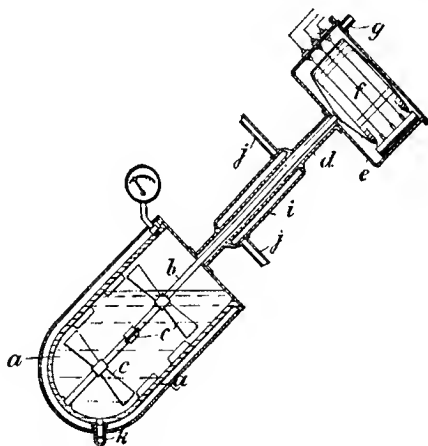


FIG. 40*n*.

type so as to avoid sparking. The gas which is to be commingled with the oil is supplied to the gas-tight inclosure by a pipe *g* which for instance may be connected to the motor chamber *e*, the gas passing from the chamber through the pipe *d* into the commingling chamber *a*. In the hydrogenation of oils this pressure is sometimes fairly high and hence the great difficulty associated with the prevention of leakage if the stirring mechanism for the shaft *b* passes through a stuffing gland. In the apparatus of Calvert there are no packing glands for any moving parts passing through the walls of the gas-tight inclosure and consequently hydrogen cannot leak from the interior of the vessel. In order to prevent vapor rising to the motor chamber *e* and to maintain this chamber fairly cool, a jacket *i* through which water circulates may be arranged on the connecting pipe *d*. The finished product is removed from the commingling chamber *a* by a pipe *k*.

Another form of the apparatus, Fig. 40*o*, has stirrers driven by an electro-magnet placed outside of the hydrogenation chamber. On rotation of the shaft

\* U. S. Patent No. 1,123,092, Dec. 29, 1914.

carrying the magnet the stirrers inside the chamber are actuated by magnetic action.

Mechanical agitation of the catalyst is effected by **Walter**,\* through the application of a magnetic field. If the catalyst itself is not magnetic it is supported on a magnetic body. By rapidly making and breaking the circuit forming the magnetic field, fresh parts of the

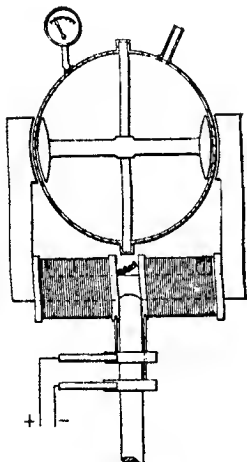


FIG. 40o.

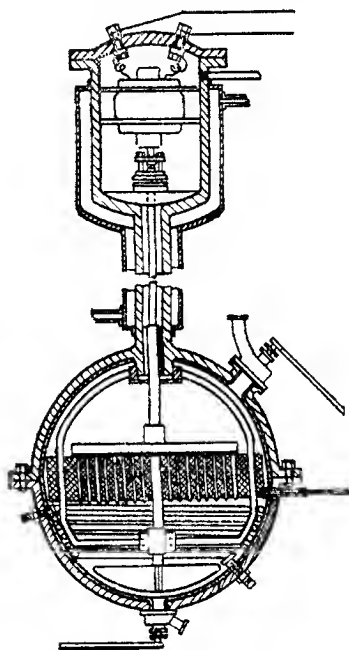


FIG. 40p.

catalyst can continually be brought into contact with the reacting substances and the catalyst can be moved to different parts of the apparatus. For reactions with gases the catalyst is supported preferably on nets or perforated plates and a magnetic field is maintained permanently near the outlet to cause the settling of any material carried along by the gas.†

By another method proposed by **Calvert** ‡ a mixture of oil and

\* German Patent No. 295,507, April 20, 1913; J. Chem. Soc. 1918, Abs., ii, 163.

† See also French Patent to Walter, No. 471,108, October 15, 1914.

‡ J. S. C. I. 1915, 434; British Patent 5967, March 9, 1914; U. S. Patent 1,142,668, June 8, 1915.

catalyst is treated with hydrogen in a closed vessel containing a rotating comb-shaped agitator surrounded by a stationary gauze screen, which finely subdivides the oil, while a centrifugal propeller at the base flings the mixture upwards to be beaten and subdivided again.

Calvert claims that improved results are obtained when, in addition to pressure, there are repeated shocks or impacts applied to the oil under pressure. Such a shock, it is alleged, cannot be applied readily by aid of a spray.

The oil is hydrogenated by subjecting a hot mixture of oil and catalyst under pressure and in the presence of hydrogen to such repeated mechanical shocks or impacts. This may be effected by means of rotary beaters. In treating oil for edible use, it is important to avoid decomposition of the fat and Calvert states this can best be done by employing high pressures of hydrogen, as such high pressures not only prevent decomposition, but they also facilitate the absorption of hydrogen by the fat. Pressures up to and above 250 lb. per square inch are used.

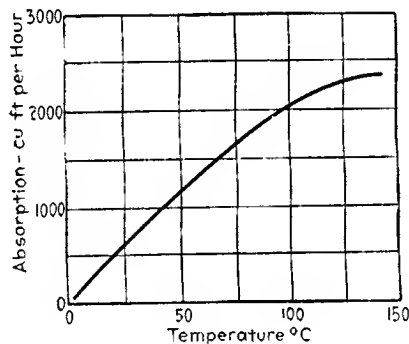


FIG. 40*g*.

The mixture of oil and catalyst is supplied to a closed container, Fig. 40*p*, of spherical form to withstand the high pressures employed, and fitted with a commingling device which imparts shocks or impacts to the oil and catalyst. This device consists of a propeller at the base and rotary agitators above, in the form of a comb. These rotary or moving parts are mounted on a shaft which is driven by a motor inclosed in a casing over the spherical container.

The temperature of operation is chosen with regard to the kind of oil to be treated. It will be found on trial, Calvert states, that there is a comparatively small range of temperature at which absorption is most active. The curve showing the rate of absorption and the temperature follows practically in a straight line till a certain point is reached, when it ceases to have an upward inclination and passes over into a substantially horizontal line. This curve is indicated in Fig. 40*g*, which is the approximate curve for fish oil. The rate of absorption, as stated, is also increased with the pressure and especially in the case of vegetable oils intended for food purposes the pressure should be high to prevent decomposition. In the latter case the pressure should be

above 250 lb. per square inch, and may be as high as 500 lb. to 600 lb. per square inch. Whale oil has been deodorized in twenty minutes, and hydrogenated to a hard fat in fifty-five minutes with the Calvert apparatus. The approach of the point of saturation can be readily ascertained by observing the absorption of the hydrogen by a suitable gauge on the hydrogen supply pipe. With this apparatus there is little likelihood of leakage of hydrogen so that the gauge gives a correct indication of the rate of absorption.

**Pictet** \* hydrogenates oil by causing it to flow by gravitation, with or without the addition of a catalyst, through a series of communicating tubes the walls of which are composed of a catalytic metal. The inner surface of the walls of the tubes is submitted to a preliminary treatment to increase the catalytic activity of the metal. Hydrogen is introduced into the tubes, and the oil is subdivided by rotating devices, which constantly brush against the inner walls.

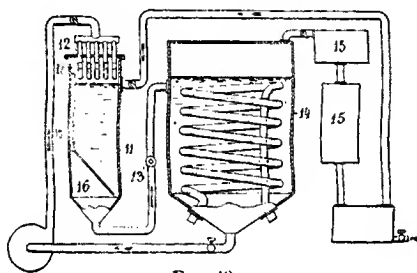


FIG. 40r.

Details of the apparatus † of **Birkeland and Devik** (see p. 36) are shown in the accompanying illustration. Fig. 40r is a hydrogenating apparatus shown in section. Birkeland and Devik state that when an efficient catalyzer, for instance pyrophoric nickel, and a good oil is employed, the hardening will be effected in from one-half to one hour.

They observe that it is advantageous to employ injectors which are so constructed that the shape or thickness of the oil jet may be altered, because such alterations during the working have proved to be necessary in order to obtain at each moment the best possible atomization and distribution of the gas in the liquid. To obtain this a member adjustable from the outside may be provided in the injector. The oil is introduced into the vessel 11 through adjustable injector nozzles 12, so as to produce a mixture of the very hot oil with hydrogen. This milky-white mixture, in which the bubbles of hydrogen are too small to be observed with the naked eye, is then introduced through

\* J. S. C. I., 1915, 434; French Patent No. 472,080, July 24, 1913.

† U. S. Patent No. 1,125,259, Jan. 19, 1915. See also Nos. 1,271,575 and 1,271,576 issued July 9, 1918 to Iltner.

a reduction valve, 13, into a larger vessel, 14. Birkeland and Devik claim to have found that under this expansion the intimate mixture of oil and hydrogen gives off malodorous volatile substances which may be condensed and washed out by passing the gas through a condensation and washing apparatus, 15. This is stated to have the advantage of eliminating several substances (volatile amines, water, etc.) before the addition of the catalyzer so that, on the one hand an unnecessary inactivation of the catalyzer is obviated, while on the other hand hydrogen is consumed only for the purpose of hardening the oil itself and not for the hydrogenation of the volatile bodies. The hydrogen gas, after having passed through the vessel, 14, and having thereupon been purified, is then again compressed and brought into circulation anew by being introduced into the hydrogen space, 18. When the oil has in this manner been freed from various malodorous volatile substances the hardening process may be started by adding the catalyzer to the oil. During the hardening operation the same circulation as before described may be maintained or the inlet to the expansion tank may be closed and the oil maintained in circulation only through the pressure vessel, 11.

Some details of Utescher's process (see page 33) are found in U. S. Patent 1,124,560, Jan. 12, 1915, where the observation appears that it has already been proposed to render fish or train oil odorless by subjecting the oil which is maintained in motion, to the action of silent electrical discharges in the presence of hydrogen.

By this means the fish or train oil is at the same time hardened, as the glycerides of unsaturated fatty acids are saturated by combining with hydrogen, and as particularly the glycerides of oleic acid are partly converted into glycerides of stearic acid. Further it has been proposed to convert unsaturated fatty acids or their glycerides into saturated compounds, by treating the fatty substances with hydrogen in the presence of a finely-divided contact metal or catalytic agent, such as finely-divided nickel or finely-divided platinum metals, and that it is his object to combine these two processes.

According to Utescher the silent electrical discharge is chiefly used for maintaining the catalytic or contact substance *permanently* active and for considerably increasing its activity. The fatty substances are either mixed with the finely-divided catalytic agent or contact substance and are then exposed in the usual manner in the form of a thin layer, to the action of silent electrical discharges in suitable apparatus, or plates of the contact metal or contact substance are arranged in a suitable manner in the apparatus, in which the silent electrical discharges take place. The rays of the silent electrical discharges are preferably allowed to impinge the surface of the contact substance or catalytic agent.

In carrying the process into effect, apparatus of the type in which the discharge itself is prevented from coming into direct contact with the fatty substances, so that solely the chemically-active rays of the silent discharges come into action may be employed; for instance Utescher states, the mercury lamp may be used. The rays from such a source are allowed to impinge on the surface of the contact substance. By means of this combined process Utescher declares it is possible to effect combination with the hydrogen, while the combined effect exceeds the effect of the total of the two agents acting separately.



The process renders it possible to effect the saturation of the unsaturated fatty acids and their glycerides, without mixing finely-divided contact metal therewith, so that the expense incurred by the recovery of the contact metal from the oil and by the regeneration of the contact substance is saved. When using metal plates in carrying out the process it is sufficient to heat the plates from time to time. The process may also be carried into effect by coating the glass tubes in which the silent discharge takes place with a thin layer of contact metal and by arranging plates of contact metal in the reaction space.

The action of the electric rays on contact metals is such that catalyzers are said to retain an increased activity even after the oil treatment rendering it possible to also carry the process into effect, by first subjecting the metal to the action of electric rays and by using the thus prepared metal as a contact substance during the treatment of the oil with hydrogen.

In order to render the metal active it is subjected to a cathode atomization treatment in an atmosphere of hydrogen. The method of procedure is as follows: the metal plate which is to serve as contact substance or catalytic agent is used as cathode in the atomization process. A pin of metal is used as anode. The chamber is first evacuated, whereupon hydrogen which has previously been carefully dried is introduced. The electric current is then passed through while at the same time a continuous slow stream of hydrogen traverses the apparatus. During the evacuation care must be taken that no traces of oil or fat vapor penetrate into the vessel, as these would deposit on the metal and cause difficulties. As by this treatment a high chemical activity is said to be imparted to the metal, air must not be allowed to enter the vessel immediately after the completion of the atomizing operation as this might cause oxy-hydrogen gas explosions. The hydrogen must first of all be displaced by nitrogen. As soon as the activity of the metal has disappeared, after having burnt off the fat, it need only be subjected to a renewed treatment as above.

**Walker \*** claims the combined application of a high-tension electrical discharge and catalytic material in the hydrogenation of oils.

According to his method a receptacle is provided containing a hollow metallic plate which is capable of being heated, on which plate the catalytic agent is supported. Nickel or nickel oxide is recommended as catalytic material. The hollow plate also serves as an electrode. Near this electrode is mounted a second electrode. Oil is projected against the heated plate by means of hydrogen acting as an atomizing agent, the finely-divided oil particles being allowed to impinge upon the heated plate while an electrical discharge is maintained between the electrodes. Referring to Fig. 408, 1 is the receptacle and 2 the hollow metallic plate provided with an inlet pipe 3 and an outlet pipe 4 by means of which superheated steam is passed through the hollow plate. The plates 5, 5', together constitute a compound terminal electrode cooperating with the electrode 2. 6 is a source of high-tension current. One of the leads 7 from this source connects with the electrodes 5, 5', while the other lead 8 connects with the hollow plate 2. An injector 10 is maintained at 9 in the walls of the receptacle. By means of this injector, hydrogen and oil under high pressure is caused to impinge upon the plate 2, contacting with the finely-divided catalytic agent. The latter may be supported by means of channels or corrugations in the face

\* Chem. Abs. 1915, 729; U. S. Patent No. 1,123,962. January 5, 1915.

of the plate. The high-tension electrical discharge passes from one electrode member to the other, through the space between the electrodes, acting on the hydrogen and finely-divided oil traversing this space. Walker claims that reaction results through the combined influence of the electrical discharge and the catalytic agent. It is stated by Walker that hydrogenated oil is secured in this manner, without the injurious results which often follow from subjecting oil to "the extended application of heat."

**McElroy\*** describes a process of hydrogenating oils with apparatus shown in Figs. 40*t* and 40*u*, as follows:

A tank is provided with a steam-heating coil and hydrogen inlets and outlets. In the top, on the right-hand side, is an oil-charging

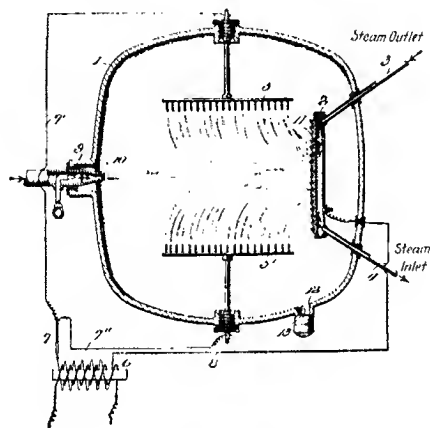


FIG. 40s.

pipe. On the top is situated a housing containing a pump or blower, the latter being arranged to draw in hydrogen from a point just below the top of the tank and to propel it to the bottom. The hydrogen discharges at that point through a revolving distributor shown in Fig. 40*u*. There is a pressure-equalizing opening in the housing floor. The tank is filled with oil to the level indicated. A screen is placed above the oil-level to serve to break up bubbles or foam. Nickel on pumice or coke is suspended in the oil and the contents of the tank are raised to 150° to 200° C. A pressure of hydrogen of five or six atmospheres is attained and the gas is caused to circulate from top to bottom by means of the blower in the housing. The discharge of hydrogen through the distributor causes the latter to rotate and sweep the bottom free of catalyzer.

\*U. S. Patent No. 1,157,993, October 26, 1915.

In a hydrogenation system involving the bubbling of hydrogen gas through a body of oil carrying catalytic material in suspension, the hydrogen may be transferred from one gas-holder to another, passing through the oil, while undergoing such transference, according to Ellis.\* In order to secure a better utilization of the hydrogen, it may be preheated by passing through a heat interchanger through which hot hydrogen issuing from the converter is conveyed.

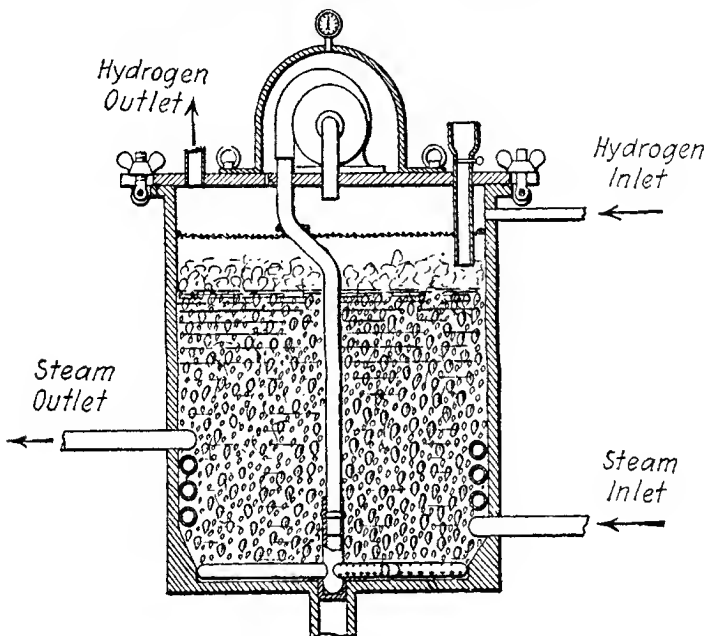


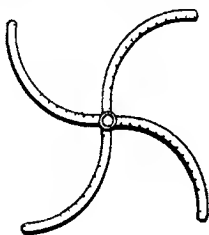
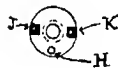
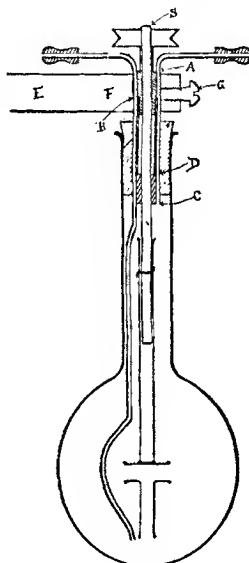
FIG. 40f.

An apparatus has been devised by E. Emmet Reid † and used for the study of catalytic hydrogenation, but may serve for the study of any reaction in which a gas is to be brought into intimate contact with a liquid under constant conditions. The problem is to introduce a high-speed stirrer, inlet and outlet tubes, and, possibly, a sampling tube through a comparatively small stopper and to render the whole gas-tight for both increased and reduced pressure. The apparatus is shown in the sketch in section, Fig. 40v.

\* U. S. Patent No. 1,247,095, November 20, 1917.

† J. Am. Chem. Soc., 1915, 2112.

The bearing,  $AC$ , is made of two pieces of steel rod,  $AB$ , and  $BC$ , 0.5 and 1.5 in. long, respectively. Both of these have a  $\frac{1}{8}$ -in. hole drilled longitudinally through them, then the longer one is drilled out to a size of about  $\frac{3}{4}$  for most of its length, i.e., from  $B$  to  $D$ . The shorter piece is turned down for half its length till it fits closely into the other, so that a double bearing is formed, with an enlarged cavity in the central portion. The two parts are assembled and channels about  $\frac{1}{16}$  by  $\frac{1}{16}$  in. are cut in opposite sides as shown at  $J$  and  $K$  in cross-section in Fig. 40*u*. Care must be taken that the channels do not cut through the walls of the cavity. The  $\frac{1}{8}$  brass tubes that are used for the gas inlet and outlet tubes are laid in these channels which are then filled with

Fig. 40*u*.Fig. 40*v*.Fig. 40*r*.Fig. 40*p*.

solder, the solder more than filling the channels. The excess of solder is turned off in the lathe so that the whole is a perfect cylinder externally and adapted to make a tight joint when passed through a cork.

The stirrers may be of any suitable form, but the Witt centrifugal stirrer shown is one of the best, as when run at high speed, it effects very thorough mixing. The stirrer may be made of glass and fastened to the shaft by a bit of wire which passes through a hole in the shaft and through holes in the stirrer. The shaft,  $S$ , is of  $\frac{1}{8}$ -in. drill rod and carries a pulley of suitable size. The inlet and outlet tubes are bent as shown and carry enlargements so as to make convenient joints with rubber tubing.

The bearing passes through a hole in a 0.5-in. rod,  $F$ , and is held in place by a set screw,  $G$ . This rod is conveniently clamped to a laboratory iron stand.

To assemble the apparatus, the shaft is pushed a short distance into the

In a hydrogenation system involving the bubbling of hydrogen gas through a body of oil carrying catalytic material in suspension, the hydrogen may be transferred from one gas-holder to another, passing through the oil, while undergoing such transference, according to Ellis.\* In order to secure a better utilization of the hydrogen, it may be preheated by passing through a heat interchanger through which hot hydrogen issuing from the converter is conveyed.

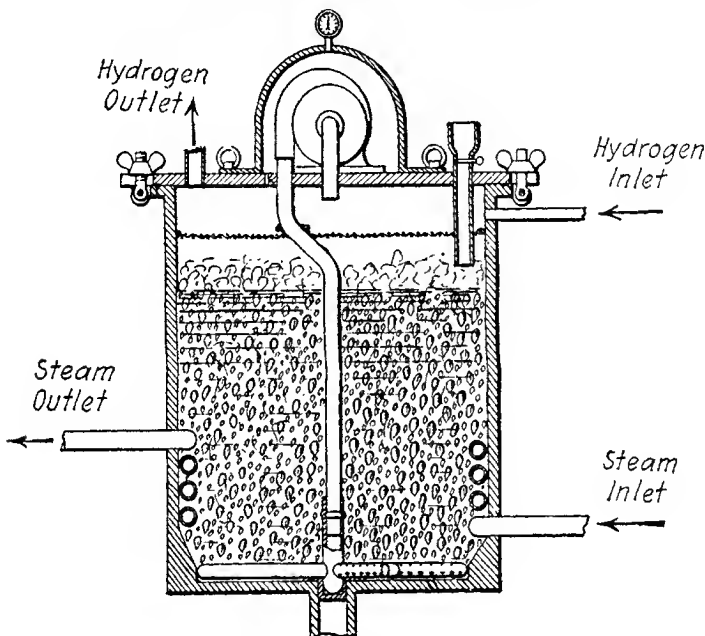


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\* U. S. Patent No. 1,247,095, November 20, 1917.

† J. Am. Chem. Soc., 1915, 2112.

well as carbon monoxide. Owing to the evolution of carbon dioxide or carbon monoxide or both, considerable pressures are generated.

Higgins suggests the following

1. Nickel formate as the reducing agent and the catalyst 2. Zinc formate as the reducing agent together with a known catalyst. 3. Zinc formate as the reducing agent admixed with palladium chloride which under the conditions of working is converted into a catalytic substance by the action of the zinc formate.

The heating must be conducted with care, as local superheating may cause spontaneous formation of oxalate from the formate and is liable to produce explosion. For this reason the apparatus must be provided with necessary safety devices.

The reaction can be conducted practically quantitatively, but for commercial purposes an excess of the reagent over the theoretical amount necessary is preferably employed. The materials taking part in the action should be dry.

The temperature may vary with the formate or mixture of formates or other reagents employed, but in general may be in the neighborhood of 20° below the point at which the formate used, spontaneously decomposes to the oxalate under the pressure existing in the apparatus at the time of so heating.

Experiments by **Kalnin** reported by Bergius\* have shown that hydrogenation is effected by heating oleic acid with alkali at 300° C. in hydrogen under a pressure of thirty atmospheres.

As the process is not a catalytic one, it is independent of the purity of the oil or the hydrogen. Simultaneous hydrogenation and saponification, in the absence of catalytic agents Bergius believes will probably prove a cheaper process than that in use. Commenting on this process, the author† observes that it is proposed to put this hydrogenated and more or less saponified product directly into the soap kettle and work it up into soap. The high gas pressure required is a drawback from the commercial standpoint.

**Barbe** and **De Paoli**‡ describe a process for the transformation of liquid into solid fatty acid, which is carried out in the following manner:

Oleic acid is introduced into a suitable lead-lined apparatus provided with a stirring device and a lead coil, which latter, by means of a two-way cock, may be caused to act either as a heater or as a refrigerator. The temperature is held below 40° C., and equivalent molecular quantities of concentrated sulphuric acid of 66° B<sub>5</sub> are introduced and stirring is continued until development of sulphurous anhydride ceases. By these means the transformation of the oleic acid into sulpho-iso-oleic and sulpho-oxystearic acids is effected, which acids are decomposed by simple boiling in water into sulphuric acid. It happens, however, that during the long boiling in the presence of sulphuric acid, necessary to decompose the sulpho-acids, the iso-oleic and oxystearic acids are dehydrated, thus giving the corresponding lactones and anhydrides. These have a relatively low melting-point (about 25° C.). It is, therefore, necessary to restore the water

\*Zeitsch f angew. Chem., 1914, 524.

†Oil, Paint and Drug Reporter, October 26, 1914, 18.

‡British Patent No. 24,837, May 5, 1908.

to the anhydrides and convert them again into acids, which is easily effected by saponification. The mixture is saponified by ammonia and treated with cold water in order to separate the oleic acid. The ammonia used for the saponification is eventually recovered by boiling. By proceeding in this manner Barbe and De Paoli have obtained from oleic acid as much as 65 per cent of fatty acids having a melting-point of 70° C.

The benefits to Germany of the hydrogenation process are referred to in an article by Hugo Schwetzer,\* who states that the cheap and practical methods which were evolved by the military authorities for the generation of hydrogen are now utilized in one of the industries which has recently become of the highest importance, namely, the manufacture of what are called "hardened oils and fats." By treatment with hydrogen, oils and fats in the liquid state are converted into solid materials, which usually command a higher price for technical purposes, such as the manufacture of soap, etc.; and low-class fatty substances, which are not fit to be eaten on account of their appearance or odor may be transformed into valuable food materials. It must also be noted that the cheap production of hydrogen is one of the prominent features in the manufacture of sulphate of ammonium according to the Haber process. Thus the manufacture of hydrogen, while originated for military purposes, he claims is helping to feed the nation by providing new edible substances, on the one hand, and a new source for fertilizers on the other.

A laboratory method for the hydrogenation of oleic acid is described by Dubovitz † The hydrogen employed is prepared from arsenic-free zinc and is purified by passing it successively through a mixture of ferrie oxide and sawdust, potassium bichromate and sulphuric acid, sodium hydroxide solution, a tube containing palladium, and concentrated sulphuric acid. Catalyzer is prepared by dissolving 50 grs. of nickel nitrate in hot water, adding pumice stone washed previously with hydrochloric acid and ignited, evaporating the mixture and igniting the residue in a nickel basin until all nitric acid has been expelled. The ignited residue is then packed into a tube 163 cm. in length. Oleic acid, dried previously at 110° C., is contained in a flask connected with one end of the tube. The air is exhausted from the whole apparatus, and hydrogen is passed through the oleic acid heated at 270° C. The tube containing the catalyst is heated at 300° to 350° C., the nickel oxide therein having been reduced in a current of hydrogen under reduced pressure at 100° C. The hydrogen bubbling through the oleic acid carries with it a quantity of oleic acid vapor (a low pressure being maintained in the apparatus) and the gaseous mixture passes into a tube containing the catalyzer, where hydrogenation of the oleic acid takes place.

Successful results are said to depend on (1) the purity of the reagents

\* Popular Science Monthly, December, 1914, 587.

† Seifen. Ztg., 1915, 304; J. Chem. Soc., 1915, 1049; J. S. C. I., 1910, 127.

used in making catalyzer. (2) The construction of apparatus. (3) The skill and experience of the chemist.

The distillation of fatty acids by means of hydrogen as carried out by Dubovitz is not regarded by Normann as having any features of novelty.\*

Robson † advances the interesting statement that there is, "as the natural consequence of the inconclusive litigation which has cost thousands of pounds and has been practically settled out of court, so far as it has been settled, a great deal of secrecy connected with the processes and such printed accounts of the processes and so far as are permitted to appear in technical literature are carefully non-committal. Many stories are told as to the way in which the nickel is used. Some say it is used as dust, some that the oil is forced through tubes packed with thin nickel wires parallel to the length of the tube, others again that the nickel itself is made into tubes, forming long circular worms, which are supplied with the necessary heat from outside, or through which the already-heated oil is passed. No one knows except the superior officers of the factory."

Contrary to the observations of others, Arnold ‡ asserts that in hydrogenating fats and oils it has been found that the mere passing of the hydrogen through the fat or oil does not cause the gas to be readily absorbed, and that a more intimate mixing will greatly reduce the time required to produce the desired reduction.

The apparatus illustrated in Fig. 40y is stated to be particularly desirable for producing the required intimate mixture and to greatly reduce the time required for the treatment. The mixing of the oil with the gas is accomplished by imparting a rotary motion to the oil in the lower portion of the tank and causing the whirling liquid to be thrown upwardly into the space occupied by the gas, by means of blades

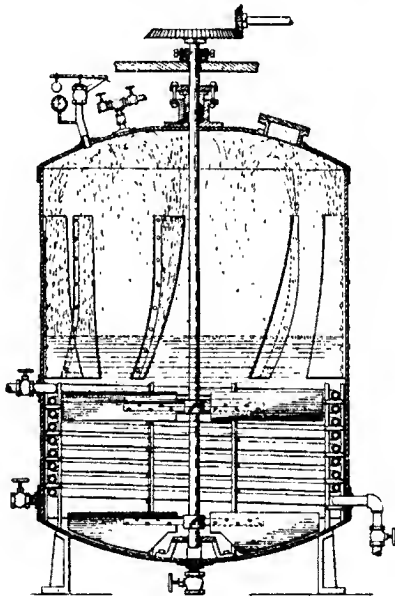


Fig. 40y.

\*Seifen. Ztg., 1915, 398.

† Drugs, Oils and Paints, 1914, 211.

‡ U. S. Patent No. 1,181,205, May 2, 1916.



or deflectors which depend into the liquid. The oil is thrown violently against the top of the tank so that it is broken up and descends through the gas space in a shower, thus causing all portions of the liquid to come into intimate contact with the gas.

**Hoehn\*** considers agitation of fatty material in the hydrogenation process to be undesirable.

He observes that violent agitation of the fatty material or oil possesses marked disadvantages, chief among which may be mentioned the bubbling of the hydrogen in or through the oil or fatty material, and that the best results are obtainable by subjecting a mass or "lake" of the fatty material or oil having the finely-divided catalytic agent in suspension, and having a relatively large exposed area or surface and a substantial depth, to the action of an atmosphere containing hydrogen. In Fig. 40z a tight housing encloses a series of pans

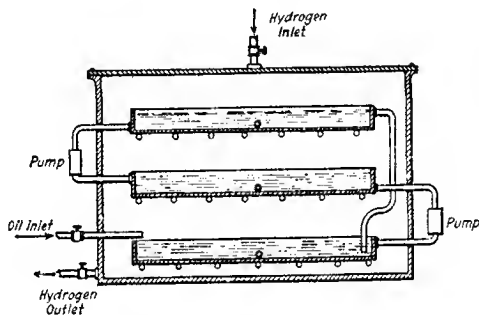


FIG. 40z.

in which the oil is exposed to the gas. The oil enters the lower pan and is pumped successively to the intermediate and upper pans, finally returning to the lower pan. The saturated oil may be drawn off from any one of the pans through outlets near the bottom (shown in the drawing midway of the pan).

For hydrogenating oils, **Lane †** proposes apparatus consisting of a vertical cylindrical vessel which is heated by means of a steam jacket or otherwise. Beaters rotating horizontally round a central vertical shaft, alternate with annular sloping shelves on the sides of the vessel, so that the oil entering at the top is alternately sprayed outwards to the sides and guided to the center of the beaters next below, and so on until it reaches the bottom; it is then pumped again to the top of the vessel.‡

\* U. S. Patent No. 1,189,817, July 4, 1916.

† British Patent No. 968, Jan. 21, 1915; J. S. C. I., 1916, 642.

‡ See also French Patent No. 481,504, Dec. 13, 1916; Chem. Abs., 1917, 3122.

**De Hemptinne's** process for eliminating the odors of fish oils \* consists in submitting the oil to the action of the silent electric discharge in an atmosphere of hydrogen.

The hydrogen is fixed by the oil and after a sufficiently prolonged action of the silent discharge, the characteristic odor is gradually modified and disappears. At the same time, the oil becomes thicker. The latter fact is due not only to the fixation of the hydrogen, but also to a conversion of the oil under the influence of the silent discharge. The elimination of the odor of fish oil may however, be effected in any gaseous atmosphere: (1) because the oil is modified by the action of the silent discharge, independently of the action of hydrogen introduced from an outside source; (2) because the silent discharge always decomposes some of the oil, so that more or less hydrogen is evolved, which is again fixed by the oil. In this way, even when operating with other gas, there is still an effect due to hydrogen. Analysis has shown that after some time, when operating with air, the gaseous mixture was composed as follows: 10 per cent of carbon dioxide, 20 per cent of hydrogen, and 70 per cent of nitrogen. The conclusion is that the elimination of the odor of fish may be effected in any atmosphere; but it is effected more rapidly and above all, more efficiently, in an atmosphere of hydrogen. Fig 40aa shows apparatus used by de Hemptinne

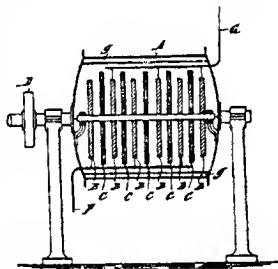


FIG. 40aa.

A quantity of the oil is introduced into a cylinder, *A*, in which are arranged on a shaft a series of parallel plates, alternately of metal *B* and of glass, or other insulating material, *C*. These plates are several millimeters distant from each other. The metal plates of odd numbers in the series are connected together and with one of the poles of a source of electricity by a wire, *F*; similarly, the plates of even numbers are connected together and with the other pole by a wire, *G*.

The cylinder is rotated by means of a pulley, *D*, and owing to a number of gutters *g* fixed to the interior of its wall, the oil is continually sprinkled over the upper part of the plates and thus forms on them a thin and mobile layer. The cylinder being filled with hydrogen, for instance, the silent electric discharge is caused to pass. The gas is fixed by the oil and gradually removes its odor. From time to time the apparatus is stopped to introduce a fresh quantity of hydrogen corresponding with the gas that has been fixed. The apparatus is provided with the cocks necessary for the introduction of gas and for the withdrawal of the oil.

**Solomonoff** † sets forth a process of hardening fats, stearic acid, palmitic acid and other fatty acids, naphtha acids, commonly known as sludge acid, waxes and the like, the object of which besides raising the melting-point is to make the material amorphous so that it may be used for the manufacture of candles; also for the purpose of render-

\* U. S. Patent No. 852,662, May 7, 1907.

† J. S. C. I., 1911, 1125; U. S. Patent No. 1,002,186, August 29, 1911.

ing stearic acid and similar materials harder, so that they may be used for insulating and other purposes. To this end, the fatty material is treated with anhydrous ammonia or other anhydrous alkali.

An example is as follows. Powdered fatty acids are mixed with ammonia, by passing through the fatty acids a stream of ammonia gas, or they are mixed with dry alkalis or salts of alkalis for five or six hours. If salts of volatile acids are used, they give off the acids and form dry salts of fatty acids. These salts are thus mixed with uncombined free fatty acids. If salts of weak non-volatile acids—for instance, ammonium borate—are used, they form the same salts of fatty acids. The resulting salts can be separated from free boric acid by melting the product; boric acid goes to the bottom. The quantities of alkalis used are different according to their nature and to the desired product. Dry ammonia may be used in amounts ranging from 0.5 to 4.55 per cent. The more ammonia or salts used, the higher the melting-point of the resulting fatty body.

Derivatives of trimethylamine, applicable in the manufacture of soaps, candles, and in general as a stearine substitute, are prepared according to **Herzmann**\* by allowing trimethylamine to act upon the chlorohydroxy fatty acids or sulphuric acid esters of hydroxy-fatty acids, such as Turkey red oil, and then the reaction mixture is heated under pressure to about 120°.

The union of unsaturated fats with trimethylamine by the Herzmann method is facilitated by pyridine or copper reduced from the oxide on an asbestos support. Soaps prepared from the fatty product are of good quality. The process yields fats of high melting-point and the investment for plant, in comparison to that required for hydrogenation, is very low †.

**De'Conno** ‡ observes that the action of ammonia or fatty aromatic amines on the higher fatty acids has never received careful scientific study, although some technical experiments have been made on the action of ammonia on fats. In ethyl alcohol under pressure ammonia decomposed glycerides to give the amides. Some patents have been taken out for the formation of anilides, by the action of aniline on fats, in this way. However, no systematic study of the formation and properties of the numerous amides of higher fatty acids, with the idea of finding derivatives having properties more useful for identification than those previously known, had been carried out. De'Conno obtained solid products which were well crystallized and easily purified, by the following method of preparation. Equimolecular amounts of higher fatty acids and aromatic amine are intimately mixed and heated in a sealed tube at 230° for five hours after evacuation with a mercury pump. After cooling the crystalline mass is purified by crystallization from 96 per cent ethyl alcohol, after treatment with animal charcoal. In this way the amide is obtained as white needle-like crystals or pearly scales. Most of the oleic amides and linolenic anilides are oils.

\* German Patent No. 275,344, June 15, 1911.

† Seifen. Ztg., 1914, 442.

‡ Univ. Naples, Gazz., chim. ital., 1917, 47, I, 93; Chem. Abs., 1918, 1172.

Hydrazine hydrate has been found by **Falciola and Mannino** \* to react with fats, forming solid products.

When hydrazine hydrate (90 or 50 per cent solution) is added to olive oil, a turbidity is produced which separates after a few hours as a more or less concrete mass, depending on the amount of hydrazine used; the action takes place in the cold without appreciable development of heat and with slight ammoniacal odor, which soon disappears. The greater part of the white solid substance thus produced dissolves in warm alcohol, from which it crystallizes on cooling. The solidifying point is about 105° C. Other oils behave similarly. Triolein treated with excess of 90 per cent hydrazine hydrate rapidly softens and hardens. Tristearin gives a similar product, m.p., 112° to 114°, and tripalmitin yields a body of m.p. 108° to 109°.

#### ELADIN

Many years ago considerable attention was paid to the production of hardened fats by the transformation of olein into eladin. Among these proposals are those represented by British Patents as follows:

Name	Patent Number.	Date.
Cambacérés . . . . .	1806	1860
Bryant . . . . .	2675	1860
de Bassano . . . . .	1099	1861
Tolhausen . . . . .	2127	1861
de Bassano and Brudenne . . . . .	2726	1861
La Peyrouse . . . . .	1385	1862
Barnes . . . . .	817	1863
Morgan-Brown . . . . .	3021	1874

See also U. S. Patent to McCarty, No. 292,669 dated January 29, 1884.

The effect of pressure and temperature on hydrogenation is discussed by **Brochet** † who does not regard a high pressure of hydrogen to be necessary in most hydrogenating operations, although in practice the employment of pressure may be useful.

In all cases a much lower temperature may be employed than that adopted in the method of Sabatier and Senderens. The proportion of nickel (obtained by reduction of the oxide at about 300° C.) may be as low as 0.1 to 0.5 per cent of the weight of liquid in some cases. The method is applicable to the hydrogenation or reduction of various organic compounds. A mixture of the active metal and the liquid (the substance to be treated, or its solution or suspension in a suitable liquid) is agitated vigorously in presence of hydrogen at ordinary or higher pressures.

Referring to the hydrogenation of fatty oils by contacting the oil and catalyzer with hydrogen, Brochet states that it was not foreseen that this process might be applicable to products other than fatty bodies, as, generally speaking, it was believed that the moistening of the catalytic metal completely checked the reaction.‡

\* Ann. chim. applicata 2, 351-6, 1914; Chem. Abs., 1915, 866.

† Compt. rend., 1914, 158, 1352.

‡ British Patent No. 16,936, 1913.

The method is stated to present the following advantages:

1. It permits of the utilization of the hydrogen at a temperature which may be much lower than the boiling-point of the product treated, which affords the advantage that, on the one hand, products non-volatile at the reaction temperature can be employed, while on the other hand hydrogenation can be effected at a relatively low temperature. It is therefore possible, Brochet declares, to obtain products that have never hitherto been obtained and to avoid the formation of undesirable products, and, by suitably selecting the temperature for the operation, it is also possible to obtain the desired body in a state of great purity. With phenol and nitrobenzene, the hydrogenation in the first and the reduction in the second place take place below 100°.

2. Products infusible at the reaction temperature but soluble either in water or in an appropriate liquid, such as ethyl alcohol, amyl alcohol, cyclohexanol, glycerine, and so forth, or insoluble products maintained in suspension in a vehicle can be hydrogenated.

EXAMPLE 1. One per cent of reduced nickel (obtained from oxide, carbonate, etc.) is added to the phenol. It is placed in an apparatus heated to approximately 100° to 120° C., and subjected to the action of hydrogen acting at a pressure of from 10 to 15 kilogrammes per square centimetre. Agitation is effected in such a manner as frequently to renew the contacts between the gas and the metal impregnated with phenol. The hydrogen is rapidly absorbed; if the supply of hydrogen is cut off, the apparatus having previously been exhausted of air, it is found that a vacuum forms in the apparatus. In this manner the phenol is transformed into cyclohexanol and by reason of the low reaction temperature, neither the formation of cyclohexane nor of cyclohexanone is observed. The filtered liquid is subjected to distillation and the catalyst is utilized for a fresh operation.

EXAMPLE 2. One kilo of paranitraniline is dissolved in a kilo of amyl alcohol and 1 per cent of reduced nickel is added. The mixture is subjected to the action of hydrogen at 120° to 130° C., and at a pressure of 10 to 15 kilogrammes per square centimetre and agitated continuously. The reaction is very rapid and the catalyst is separated by filtration, and the paraphenylenediamine crystallized by cooling.

In these two examples the absorption of the hydrogen is theoretical, so that the end of the reaction is noticeable by cessation of absorption.

Brochet and Bauer\* have hydrogenated a number of aromatic compounds containing an ethylenic linkage in the side chain and one aliphatic compound. 1. Octene readily yields octane. Cinnamic acid, its sodium salt, and its methyl ester yield phenylpropionic acid and its corresponding derivatives. The hydrogenation proceeds better with the sodium salt than with the free acid, but the conversion readily takes place on using the sodium salt. Anethole, eugenol and safrole readily undergo hydrogenation at 60° to 80° C., while for isoeugenol ordinary temperature suffices. Brochet and Cabaret† find that the substances containing aliphatic ethylenic linkage which were hydrogenated in the presence of active nickel under a slightly increased pressure by Brochet and Bauer also undergo hydrogenation under atmospheric pressure, but in this case the reaction takes place far more slowly and requires a larger amount of the catalyst.

\* *Comptes rend.*, 1914, **159**, 190.

† *Ibid.*, 326.

Brochet \* suggests a further modification by the substitution of vigorous shaking for the high pressure, 10 to 15 kilos per square centimetre, first recommended. This method is applicable generally to compounds containing acetylenic or ethylenic bonds and to some easily reducible substances such as indigo. Details are given for the reduction of sodium cinnamate to phenyl-propionate, using reduced nickel as the catalyzer and hydrogen, and for the preparation of indigo-white by reduction of indigo both by hydrogen and by water gas.

In a paper on polymerized drying oils, Morrill † states that linseed oil from various sources was thickened in bulk or in smaller quantities in the laboratory, and to avoid oxidation the operation was performed as far as possible in an atmosphere of carbon dioxide or hydrogen.

Hydrogen under ordinary conditions or under pressure without a catalyst is stated to have no action on unsaturated fatty acids, ‡ nevertheless, it was found that under the conditions of the experiments a very slight addition occurred and subsequently carbon dioxide was used instead. The oil was heated for twenty-eight to sixty hours at 260° C., and the thickened oil was completely soluble in light petroleum.

While Shuck § was carrying on some experiments on the catalytic hydrogenation of naphtha-extracted corn-oil, he observed that a sample which had not been purified sufficiently to allow the catalyzer to act and which had not hardened, nevertheless was rendered odorless and palatable by the action of the hydrogen on the oil containing a catalyzer in suspension. Although no appreciable hardening had taken place, the improvement in odor and taste was so marked that a fresh sample was treated under identical conditions except that no catalyzer was present. This sample proved to be equal in odor and taste to that treated with hydrogen in the presence of a catalyzer and thus showed that the catalyzer did not function in the removal of odor from the corn oil. Fish oil also was deodorized.

The method of deodorizing any oil or fat by this process consists of blowing hydrogen, or a gas whose principal constituent is hydrogen, through the heated oil and allowing the hydrogen with the entrained vapors from the oil to escape freely from the containing vessel until the desired result is obtained. In the commercial application of this process, the fatty acid and other fumes are condensed and washed from the hydrogen which is thus completely purified and used over again. The entire apparatus should, of course, be filled with hydrogen to the exclusion of all oxygen from the air at the time of its first use. Thereafter each new batch of oil is introduced and the deodorized oil withdrawn through pipes so that no air enters

\* J. S. C. I., 1915, 1116. Second Addition dated Nov. 19, 1913, to French Patent No. 458,033, July 27, 1912, J. S. C. I., 1913, 1031 and 1914, 18.

† J. S. C. I., 1915, 105.

‡ Thorpe's Dictionary, Oils, Fats and Waxes, 2d Ed., Vol. 3, 57.

§ Met. & Chem. Eng., 1916, 608.

the apparatus. A means of drying the hydrogen is provided in the gas-purifying system if the oil being treated contains appreciable quantities of water.

Cocoonut oil was treated by this process at the same time that some of the same oil was deodorized with superheated steam. Both samples were put in clean tins with lids loosely laid on, then alternately kept in a warm place where the oil was liquid during the day and in a cool place at night for four months. The steam-deodorized oil became rancid in a few weeks and was very poor in quality in two months. The hydrogen-deodorized oil was pleasant to taste after two months' storage.

Among the commercial possibilities of this process Shuck states that the purifying of fish oils so as to render them edible is of prime importance. Even the deodorization of fish oils for technical purposes is a matter of interest.

While not taking the place of catalytic hydrogenation of fish oils because the oil is not hardened, Sehnick considers the process very much cheaper to operate. It is claimed that fish stearine which is naturally a solid fat at ordinary temperatures can be made into an acceptable cooking fat at very low cost by this process. Fats which have been burnt from continued use in cooking and have absorbed the odor of fish, onions, garlic, etc., can be rendered perfectly bland and neutral by this deodorizing process. Likewise garbage grease and rendering-works fats can be purified and freed from objectionable odor. This latter class of fats usually contains substances that "poison" a catalyzer and therefore are not easily deodorized by catalytic hydrogenation. Medicinal castor oil, it is claimed, can be rendered entirely free from its characteristic odor and taste while still retaining its medicinal properties. A temperature of 185° C may be used.

Certain vegetable oils such as soya bean oil, not readily deodorized with steam, Shuck asserts are rendered bland and palatable by this process.\*

Schrauth† observes that Varentrapp's reaction is applicable to all unsaturated fatty acids, which in this way may be converted into saturated fatty acids containing a smaller number of carbon atoms. For example, elupanodonic acid, which is the cause of the characteristic odor of marine animal oils, is slowly transformed into saturated fatty acids and it is possible in this way to obtain up to 85 per cent of a perfectly white solid distillate from the mixed fatty acids of the oils, provided that glycerol is absent. Marine animal oils of the best quality yield tallow-like fats, which when mixed with other fats give good lathering soaps, while the fatty acids from refuse marine animal oils yield products which resemble the fatty acids of palmitic and cocoonut oils both in properties and composition.

The electrolytic reduction of organic bodies and especially fatty acids or esters is carried out by Higgins‡ with the aid of nickel or cobalt oxide or hydroxide.

\* See also U. S. Patent No. 1,260,072, March 19, 1918.

† Seifenfabr., 1915, 35, 877-879. Z. angew. Chem., 1916, 29, Ref., 31; J. S. C. I., 1916, 428.

‡ J. S. C. I., 1911, 982; British Patent No. 18,969, 1910.

The catalyzing agent may constitute the whole or part of the electrode from which hydrogen is normally disengaged, or may be in suspension in the electrolyte composed of or containing the body to be reduced. According to one mode there is formed a coherent mass composed of the oxide or hydroxide of cobalt or nickel, or a mixture of these, and a suitable, chemically inert, binding material, this coherent mass constituting the cathode. For instance the oxide or hydroxide of cobalt, or nickel, is mixed with or deposited upon kieselguhr, pumice, or other porous inert powder, and the whole formed, with or without the addition of cement, or gums, into a coherent mass by mechanical pressure; or the catalytic material may be mixed with a cane sugar solution which, on subsequent roasting in a non-oxidizing atmosphere, yields a porous mass of carbon-containing the active ingredients. Higgins also states that perforated plates such as are commonly used in secondary cells may be employed to support the catalyzing agent either alone or mixed with the binding material referred to above.

A survey and discussion of the field of hydrogenation by **van Leent**\* involves a comparison of the physical and chemical properties of cottonseed, linseed and whale oils before and after hydrogenation. Methods for the detection and determination of nickel in the products are discussed. Hydrogenation with and without high pressures showed that olive and peanut oils are especially adapted to hardening at atmospheric pressure. Linseed oil is stated to hydrogenate but very little even with platinum black as catalyst.

The hydration of unsaturated organic acids is carried out by **Schicht A. G. and Grün**† by heating salts of the acids with water in the presence of small amounts of an alkali substance, under pressure, whereby water is added directly. The double union disappears the iodine number decreases continuously and hydroxyl and ether groups are formed. E.g., 500 g. linoleic acid (iodine number, 174.0) were slightly more than neutralized with 40% NaOH, and heated in a pressure vessel for three hours to 270° to 280°. The viscous liquid reaction product showed an iodine number of 83.8.

#### SYNTHETIC ESTERS OF OLEIC AND OTHER FATTY ACID AND THEIR HYDROGENATED PRODUCTS

In 1906 **Bedford**‡ studied the esterification of linolic and linolenic acid and the hydrogenation of these esters in the presence of finely-divided nickel. The ethyl and methyl esters of these acids were prepared by him as follows:

\* Chem. Weekblad 13, 712-55, 1916; Chem. Abs., 1917, 218.

† German Patent No. 287,660, July 16, 1914; Chem. Abs., 1916, 2128.

‡ "Über die Ungesättigten Säuren des Lemöls," Dissertation, Erlangen, 1906; Ber., 42, 1909, 1324.



The free fatty acid was boiled under reflux with an excess of the alcohol in the presence of a small amount of sulphuric acid. The product was then treated with an excess of sodium bicarbonate solution. The oil that separated out was decanted off and dissolved in ether. The ether solution was washed with water, dried with anhydrous sodium sulphate and then distilled to remove the ether. The oil left behind was purified by vacuum distillation. The ethyl esters of linolic and linolenic acid were hydrogenated in the presence of finely-divided nickel at about 180° C. Ethyl stearate was obtained in both cases.

Methyl esters derived from thickened linseed oil were hydrogenated by **Morrell**\* who employed colloidal palladium as a catalyst. Stearic acid in good yield was obtained from the products of hydrogenation.

The methyl, ethyl, propyl, isobutyl, amyl, benzyl, and glyceryl esters of oleic acid were prepared in the author's laboratory.† They were all liquid at the ordinary temperature, and yielded practically saturated products when hydrogenated in the liquid state, at an increased temperature, in presence of reduced nickel. The nature of the alcohol did not seem to have much effect on the rate or degree of hydrogenation. A product derived by heating oleic acid and aniline was found to hydrogenate readily to form a very hard product.

**Methyl Oleate.** U. S. P. oleic acid (56.4 g.) was dissolved in 25.6 g. acetone-free methyl alcohol. The solution was treated with 0.7 g. sulphuric acid and then boiled for 5½ hours. The product had an acid number of 17.6. After washing with alkali the acid number of the oil fell to 1.3. The iodine number was found to be 87.0. The theoretical iodine number of methyl oleate is 85.8.

**Hydrogenation of Methyl Oleate.** A portion of methyl oleate containing 1 per cent of finely-divided metallic nickel (reduced for fifteen to twenty minutes in a stream of hydrogen at 320° to 350° C.) was treated for about two hours at about 180° to 200° C. with hydrogen which was simply allowed to bubble through the liquid as a brisk stream, thereby maintaining the catalyst in suspension. The solid product, obtained after filtration was white and crystalline. It had an iodine number of 0.4 and melted at 37° C.

**Ethyl Oleate.** Ethyl oleate containing 1 per cent of metallic nickel (reduced for fifteen minutes in a stream of hydrogen at 320° to 350° C.) was exposed to a rapid current of hydrogen for about two hours. The oil was filtered through ordinary filter paper in the hot oven. The product melted at 31° C. Its iodine number was 5.3.

**Propyl Oleate.** The hydrogenation in this case was carried out under conditions practically identical to those employed in the hydrogenation of methyl and ethyl oleate. The hardened oil had an iodine number of 1.3. It melted at 27° C.

**Iso-butyl Oleate.** The ester was hydrogenated for about two hours in the presence of 1 per cent metallic nickel (reduced for fifteen minutes at 320° to 50° C.). The temperature of hydrogenation was 180° to 200° C. The hydro-

\* J. S. C. I., 1915, 107.

† J. Ind. Eng. Chem., 1916, 1105; J. S. C. I., 1917, 39; Chem. Abs., 1917, 218. See also U. S. Patent No. 1,277,708, Sept. 3, 1918.

generated product was soft and translucent and distinctly crystalline. It somewhat resembles crude paraffine. It had an iodine value of 0.2 and melted at 25° C.

**Amyl Oleate.** This ester was hydrogenated under conditions similar to those employed above. The hydrogenated product was soft and non-homogeneous, consisting of a liquid oil and a crystalline body. It had an iodine value of 1.7 and melted at 22° C.

**Glycerine Oleate.** Oleic acid (56.4 g.) and 18.4 g. glycerine were heated for five hours at 240° C. with continuous stirring. The only product was washed several times with warm water and dried. Its acid number was 0.6. In cool weather a crystalline body formed which rendered the ester opaque. The iodine number of the product was 69.4. Pure glycerol mono-oleate has an iodine number of 71.3. The ester was hydrogenated in the usual way. Treatment with hydrogen for about two hours at 180° to 200° C. gave a product which melted at 59° C. and possessed an iodine number of 6.5. The hydrogenated product was similar in appearance to a good grade of hardened cottonseed oil, except that it was somewhat darker in color.

**Benzyl Oleate.** Hydrogenation in the presence of finely-divided reduced nickel gave a product which had an iodine value of 6.3 and a melting-point of 28° C.

**Oleic Acid and Aniline.** Aniline (24.4 g.) and 37 g. oleic acid were heated under a reflux condenser for four hours at 170° to 190° C. The mixture darkened considerably. It was steam-distilled until the distillate was free from aniline. The acid number of the steam-distilled product was 30.5. It became solid on standing. The substance was treated with a solution of sodium hydroxide and washed free from alkali and sodium oleate. The acid number of the product was reduced to 3.6. The product melted at 34° C. It was dark brown in color and had a greasy feel. The material was hydrogenated for two hours at 190° to 200° C. in the presence of 1 per cent finely-divided reduced metallic nickel. The hydrogenated product was filtered in the hot oven. It had an iodine number of 30.5. The iodine value of the unhydrogenated substance was 69.5. The iodine value of oleic anilide is 71.6. The product melted at 76° C. and was very hard and brittle.

A tabulation of these results follows.

Ester.	Acid Number	Iodine Value	HYDROGENATION PRODUCT	
			M. pt., ° C.	Iodine Value
Methyl oleate.....	1.3	87.0	37	0.4
Ethyl oleate.....	0.6	83.3	31	5.3
Propyl oleate.....	0.5	77.9	27	1.3
Isobutyl oleate....	0.4	75.7	25	0.2
Amyl oleate.....	0.7	71.3	22	1.7
Benzyl oleate.....	0.7	62.3	28	6.3
Glycerol mono-oleate...	0.6	69.4	59	6.5
(Aniline compound)...	3.6	69.5	76	30.5

In the catalytic hydrogenation of fatty acids and their glycerides, the speed of reaction is maintained constant\* by gradually raising

\* Soc. de Stearinerie et Savonnerie de Lyon and P. Berthon. British Patent No. 107,969, June 25, 1917.

the temperature and adding additional catalyst, and sudden rises in temperature are avoided by providing a heat-exchange apparatus for the hydrogen entering and leaving the reaction chamber. The hydrogen is purified and dried by subjection to a low temperature and free fatty acid distilling over is separated from the hydrogen. In an example soya oil is treated at 200°, the temperature gradually raised to 300° and the catalyst introduced little by little. In another example whale oil is treated at 170°; the reaction which is at first violent, tends to become quieter and is then revived by adding more catalyst. The amount of free acid in this product does not exceed 0.5 per cent.

The application of esterification as a means to reduce free fatty acid has been utilized by **Dreymann** \* in the treatment of oils which which cannot be readily refined by caustic alkali.

Dreymann states that the presence of even as small a quantity as 2 per cent of free fatty acid in an oil is sufficient to greatly impair the effectiveness of the catalytic agent used in the hydrogenation process. Hence it is the practice to first carefully neutralize the oil by means of caustic soda. If the amount of the free fatty acids exceeds 5 per cent, their removal by caustic alkali refining is difficult and is attended with considerable loss and expense. In consequence, Dreymann states only high-grade neutral oils are being used for hydrogenation purposes. Dreymann proposes to meet the difficulty by esterifying the free fatty acid of the oil with alcohol, which he states can be hydrogenated as readily as a pure glyceride. In this way, oils and fats containing as much as 20 per cent of free fatty acid may be hardened. Applying the process to a fatty oil containing about 20 per cent of free fatty acid, Dreymann recommends the use of 5 to 8 parts of absolute ethyl alcohol to 100 parts of the oil. A small quantity of hydrochloric acid is added to act as a catalyzer in the esterification operation and calcium chloride is introduced to serve as a dehydrating agent. Dreymann recommends 3 parts of hydrochloric acid and 20 parts of calcium chloride. The mixture is heated to a temperature of about 90° C., for three hours, after which time the product is washed with water and will then be found to have a low content of free fatty acid, in general, less than 3 per cent. This amount of free fatty acid can be readily removed by the caustic soda refining process. When the oil or fat contains 30 per cent or more of free acid, Dreymann states it is advantageous to remove the glycerine as for example, by the Twitchell process. The fatty acids thus obtained can be converted into esters by treatment with alcohol, the proportion of alcohol in this case being increased to 20 parts. He states that the esters thus produced contain only 1 to 3 per cent free fatty acid, which may be removed by refining with alkali. The application of the process to the treatment of inferior products, such as cotton oil, soap stock, and garbage grease, is recommended.

The hydrogenation of fatty material containing such quantities of free fatty acids as tend to interfere seriously with the catalytic

\* U. S. Patent No. 1,228,888, June 5, 1917.

process is carried out by **Ellis** \* by esterifying the fatty acids with glycerin.

This may be carried out by heating the oil with glycerin to a temperature between  $250^{\circ}$  and  $285^{\circ}$  C for two or three hours. The reaction mass may be kept out of contact with air by introduction of a current of hydrogen. In one case a whale oil having an acid number of about 25 was treated with 5 per cent of glycerin and the acid number was reduced to approximately 1. After the esterification stage has been completed a catalytic agent is added to the oil and the product hydrogenated at a temperature of about  $180^{\circ}$  C in the case of nickel or at a lower temperature if a catalyzer of the platinum group is employed.

An apparatus for hydrogenating oils designed by **Sugita** † consists of a cylindrical hydrogenating vessel or converter which is provided with two revolvable shafts, one within the other. A propeller with a number of nozzles for supplying hydrogen, each provided with an automatic valve, is attached to the end of one of the shafts. By this arrangement the hydrogen is made to contact rapidly and thoroughly with the oil, thereby facilitating the hydrogenation.

For the effective mixing of oil, catalyzer and hydrogen, **Ittner** ‡ recommends an apparatus of the character shown in Fig. 40bb.

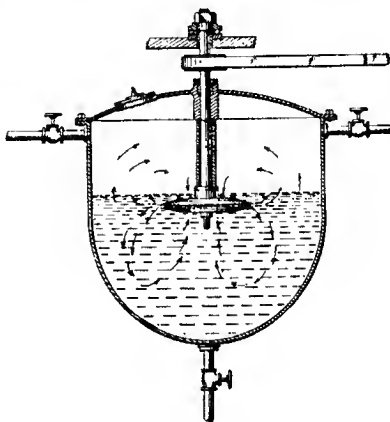


Fig. 40bb.

In this drawing a receptacle containing oil is equipped with a peculiar form of agitating and hydrogen-mixing device shown in detail in Fig. 40cc. The latter is termed by Ittner a centrifugal distributor or injector. It is set below the normal level of the oil and is so constructed that the liquid is drawn in near its centre and discharged centrifugally outward so that circulation of the liquid is effected. The upper part of the chamber is filled with hydrogen gas which may be at atmospheric pressure or under increased or decreased pressure. The gas is drawn through the hollow shaft of the centrifugal distributor by means of perforations and passes out through the disc-shaped portion admixed with oil. By this means, Ittner states, an intermixture of the liquid and gas of such intimacy is obtained that ordinary

\* U. S. Patent No. 1,261,911, April 9, 1918. See also No. 1,271,575 and 1,271,576, July 9, 1918.

† Japanese Patent No. 30,637, January 19, 1917; Chem. Abs., 1917, 2413.

‡ U. S. Patent No. 1,242,445, October 9, 1917.

agitation can add but little to the efficiency of the operation. In fact, he states it is sometimes advantageous to avoid a high degree of agitation of the liquid and screens or baffles may be so placed as to lessen agitation.

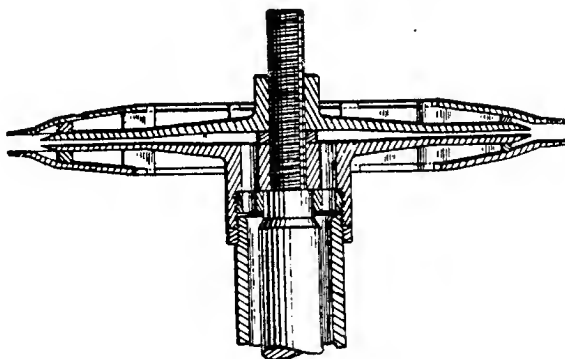


Fig. 40cc.

A method of automatic regulation of the supply of liquid to and discharge of liquid and removal of gas from pressure vessels for mixing liquid with gas is described by Noll.\*

An apparatus for bringing liquids and gases into contact with each other which is of interest to the hydrogenation industry is described by Feld†. Fig 40dd shows a simple type of the apparatus. Gas enters the stationary bell, *a*, through the pipe *c*, and is distributed through the liquid, *g*, in an atomized condition by the rotation of the agitator, *d*, which also serves to agitate and mix the liquid. Over twenty modifications of the apparatus are shown.

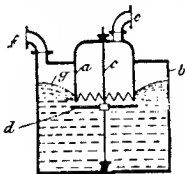


Fig. 40dd.

To remove traces of nickel from the hardened product obtained by hydrogenating fatty oils with a nickel catalyzer, Whitaker‡ recommends treatment of the hardened material with fuller's earth.

After the hydrogenated fat or oil leaves the hydrogenator or converter or after it has passed through the filter press and while still in a liquid condition, a quantity of fuller's earth is introduced. The oil agitated is therewith and the earth is then removed by filtration. Ordinarily 1 or 2 per cent by weight of fuller's earth may be added, but when a large amount of nickel soap is present in the oil, more than this quantity of the earth may be required. Fuller's earth, which has been heated to 100° C. is stated to lose its efficiency as a

\* German Patent No. 271,641, May 9, 1913; J. S. C. I., 1914, 469.

† Zeitsch. angew. Chem., Aufsatzteil, 1914, 224; U. S. Patent No. 1,110,914, September 15, 1914.

‡ U. S. Patent No. 1,242,624, October 9, 1917.

means of removing traces of nickel, so that care should be taken not to operate at a temperature at or above the point where dehydration would impair its usefulness.

A process of effecting catalytic reactions is described by **Hagemann and Baskerville**,\* according to which nickel or an alloy of nickel with a small amount of cobalt, having all or a part of its surface oxidized, is used as the catalytic body.

Instead of using the material in the form of leaves† the catalytic agent may be used in the form of wire or sheets and the like, having a very slight surface oxidation. It is stated that alloys of nickel with a small amount of cobalt when oxidized on the surface act much more vigorously as catalyzers than either pure nickel or cobalt. In preparing the sheets, wire, or other suitable shapes for catalytic use, the superficial oxidation is carried out by heating in air, oxygen, or ozone, until the metal surface ceases to be bright. The revivification of the catalyzer may be carried out by first removing any fatty material or other foreign accumulations from the sheets or wires by extraction with a solvent. The nickel basis is then dried and heated in an oxidizing atmosphere to a temperature of 300° C. or higher until oxidation has gone on to slight depth, after which the catalyzer is subjected to the action of a reducing gas, such as hydrogen, at a temperature of 300° C. to reduce the nickel oxide formed, then the material is subjected to the action of air at about 300° C. for some time, until the surface becomes coated to a greater or less extent with a thin film of oxide.

The baffle-plate principle is applied to the hydrogenation of oils by **Maxted and Ridsdale**,‡ who obtain a large reacting surface of unsaturated oil and hydrogen by projecting the mixture through a vertical column provided with fixed horizontal propeller-like baffle plates so shaped and placed in opposition to each other that the moving liquid-gas mixture is rotated alternately clockwise and anti-clockwise.

According to **Higgins**,§ an effective apparatus for hydrogenation is secured by the employment of agitators equipped with gas cups as shown in Fig. 40*cc*.

Beaters or vanes are employed with a number of conical cups closed at their bases and open at their narrower ends where they are mounted upon the plate forming the beater or vane. The plate is provided with a hole of corresponding size and the cup is mounted on the plate so that the opening in the cup is coincident with the hole in the plate. Such conical cups are uniformly distributed and are mounted upon one side of the beaters or vanes. Between the respective cups, holes are formed in the plate. These holes are advantageously arranged all over the plate so as to form continuous longitudinal and transverse rows intermediate the respective rows of conical cups. By such means,

\* U. S. Patent No. 1,238,137, August 28, 1917.

† U. S. Patent No. 1,083,930, January 13, 1914.

‡ British Patent No. 109,993, September 29, 1916; J. S. C. I., 1917, 1185.

§ U. S. Patent No. 1,170,815, February 8, 1916; Chem. Abs., 1915, 4; British Patent No. 15,063, June 30, 1913. See also Schwarzman, U. S. Patent 1,280,315.

on the rotation of the beater or vanes, the cups pass into the liquid, open end first. A quantity of the gas thus becomes imprisoned in the cups and as the beater or vane rotates the oil passes into the cup and the gas passes out. The gas continues to pass out throughout the course of the beater or vane through

the liquid. By the provision of holes intermediate of the cups, the rush of the oil through these holes carries the bubbles of gas with it, and thus the gas is brought into intimate contact with the liquid.

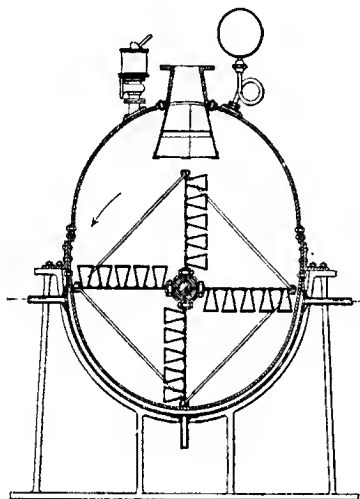


Fig. 40 cc.

The hydrogenation of various resins such as ordinary rosin, damar, sandarac, shellac, copal, pontianak, is described by Ellis.\* Nickel, copper, cobalt, palladium, or platinum may be used as catalyzers. The resin may be hydrogenated in a melted condition or in solution in an inert solvent. Petroleum or aromatic hydrocarbons may be used as the solvent material. A temperature of 180° C. is specified and a pressure of hydrogen of 10 lb. or more.

TABLE SHOWING THE COMPOSITION OF CERTAIN OILS AND FATS  
(MOORE, RICHTER AND VAN ARSDEL)

No	Material.	IODINE NUMBER		CALCULATED PERCENTAGES		
		Original Material	Liquid Fatty Acid	Saturated Glycerides	Olein	Linolin
1	Cottonseed oil . . . . .	110.7	149.5	22.6	26.9	50.5
2	Cottonseed stearine . . . . .	86.0	149.8	40.0	20.5	39.5
3	Peanut oil . . . . .	98.0	121.7	15.85	54.9	29.25
4	Corn oil . . . . .	110.6	133.0	13.0	46.0	41.0
5	Olive oil . . . . .	82.0	97.8	12.4	80.1	7.5
6	Leaf lard . . . . .	63.5	105.3	37.0	52.4	10.6
7	Compound lard . . . . .	97.0	143.0	29.3	29.1	41.6
8	A semi-solid hydrogenated cottonseed oil . . . . .	63.0	101.0	34.75	57.2	8.05

A thorough study of the results of partial hydrogenation of cottonseed oil has been made by Moore, Richter, and Van Arsdel.†

\* U. S. Patent No. 1,249,050, December 4, 1917. † J. Ind. Eng. Chem., 1917, 451.

They state that investigations heretofore have considered the unsaturated components as a whole, rather than as individual units and that they have studied the physical and chemical changes which take place in oil during the process of hydrogenation, particularly changes in the amount and character of the various fatty glycerides, and the effect of variable factors, such as temperature and pressure.

### I. HYDROGENATION CURVES

For the study of the glyceride change during hydrogenation, the tests made on samples included iodine number and iodine number of liquid fatty acids, calculation giving the "component glycerides" (olein, linolin and saturated glycerides) of each sample. The smooth curves drawn through the points plotted on triangular diagrams always, in the cases studied, had the same general shape, suggestive of the hyperbola, concave toward the right-hand side of the triangle. The linolin is always found to decrease from that present in the original oil and the saturated glycerides always increase, while the olein rises to a maximum and then falls continuously. These changes are what would be expected, since hydrogenation must cause linolin to disappear, forming olein, while olein, hydrogenating more slowly, would at first increase and then eventually disappear, forming stearin, a saturated glyceride. The shape of the curve depends upon the relative velocity of these two actions, and it appears that this relative velocity must be subject to important variation, according to the experimental conditions.

**Effect of Temperature.** The result obtained in Fig. 40ff may be interpreted as follows: while both linolin and olein were hydrogenated faster at the high temperature than at the low temperature, relatively linolin was hydrogenated much faster at the high temperature, so that the olein had a greater tendency to accumulate under the latter conditions. In other words, both unsaturated radicals are acted upon in both cases, but at the higher temperature the more highly unsaturated one comes nearer to being *singled out* for hydrogenation than at the lower temperature—the action is more "selective." This would be the case if, for instance, the temperature coefficient of the reaction linolin-olein is greater than that of the reaction olein-stearin, but in view of the complicated nature of the glycerides which are actually present that explanation is doubtless too superficial to be the entire truth.

**Effect of Pressure.** The influence of the hydrogen pressure upon the course of the hydrogenation may be illustrated by Runs C and D (Fig. 40gg).

Increasing the pressure is here seen to have the opposite effect to increasing the temperature, so that at a high pressure the action is less "selective" than at a low pressure. An obvious corollary of this conclusion is that it would appear to be possible to duplicate at high pressure and high temperature a curve obtained at low pressure and low temperature, while the reaction as a whole might be made to proceed many times as fast in the former experiment as in the latter.

In this case again a tentative "mechanism" may be put forward. It should first be noted that the occasional hydrogenation of a linolin chain clear to stearin instead of only to olein would have the same apparent effect as would an increase in the relative velocity of the olein-stearin reaction. Now if an increase in



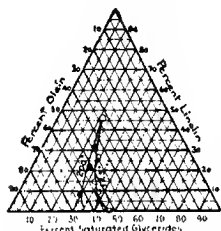
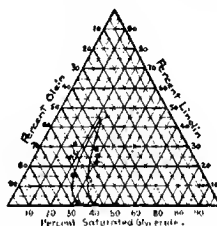
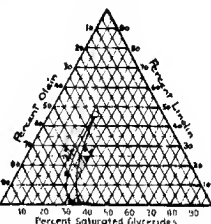
TABLE OF TESTS FOR HYDROGENATION CURVES, EMPLOYING COTTONSEED OIL  
 Abbreviations: LFA, Liquid Fatty Acids; SG, Saturated Glycerides; Ol, Olein; Lin., Linolin

EXPERIMENTAL CONDITIONS DURING RUNS.												
Apparatus	Run.	Temp.	Pressure.	Catalyzer	Agitation.	Oil Used	Iodine No			PERCENTAGES		
							Sam- ple	Fat	LFA	SG.	Ol.	Lin.
Glass	A	125°	Atmos.	5% No. 1	Bubbling	...	A0	107.8	143.9	21.7	32.3	46.0
	B	200°	Atmos.	5% No. 1	Bubbling	...	1	84.5	124.6	29.0	44.2	26.8
							2	70.5	110.2	33.1	52.2	14.7
							3	61.9	103.4	37.5	53.1	9.4
Iron	C	155°	20 lb.	2% No. 1	135 R.P.M.		C0	45.8	87.7	46.9	53.1	...
	D	155°	40 lb.	2% No. 1	135 R.P.M.		1	107.7	143.9	21.7	32.3	46.0
							2	59.8	92.3	32.4	65.9	1.7
							3	50.3	88.0	41.6	58.4	...
Iron	E	155°	20 lb.	4% No. 1	135 R.P.M.		E0	107.7	143.9	21.7	32.3	46.0
	F	155°	20 lb.	2% No. 1	250 R.P.M.		1	77.2	112.0	27.9	54.4	17.7
							2	57.6	92.4	34.8	63.3	1.9
							3	42.9	86.4	50.3	49.7	...
Glass	G	160°	Atmos.	No. 2	Bubbling		G0	110.9	149.1	22.4	27.2	50.4
	H	160°	Atmos.	No. 2	Grate doubled		1	88.4	125.1	26.2	45.3	28.5
							2	79.6	118.5	29.8	48.2	22.0
							3	75.0	113.3	30.8	51.4	17.8
Iron	I	155°	40 lb.	2% No. 1	135 R.P.M.	10 lb.	5	71.7	108.8	31.0	54.9	11.1
	J	155°	40 lb.	2% No. 1	135 R.P.M.	20 lb.	6	68.8	104.7	31.3	57.1	11.0
							10	108.4	142.8	20.6	33.5	45.9
							1	97.4	130.6	22.1	43.4	34.5
(Run I in container 25 in. long and 12 in. in diameter)							2	78.9	112.6	26.8	55.5	118.1
(Run J in container 40 in. long and 16 in. in diameter)							3	66.8	101.3	31.2	60.3	8.5
							4	51.0	91.6	41.8	57.3	0.9

Catalyser No. 1, Green nickel oxide reduced in hydrogen 4 hours at 320-340° C. pressure 30-60 lbs. Catalyst No. 2, Basic nickel carbonate and infusorial earth, calcined and reduced in hydrogen at 400-360° C., 4-14 hrs. at atmospheric pressure.

hydrogen concentration at the catalyzing surface (such as would be produced by increased pressure) caused an increase in the number of linolin chains to which four atoms of hydrogen were added at once, the observed effect would follow.

**Influence of Percentage of Catalyst.** The influence of percentage of catalyst was illustrated in Experiments *C* and *E* (Fig. 40*hh*). In this case the observed result, which shows a divergence in the same direction for increased percentage of catalyst as for increased pressure, seems to be at variance with what is commonly understood to be a law of catalytic reactions, namely that if the amount (or surface) of the catalyst be increased, all of the reactions involved will be speeded up by exactly proportional amounts. In this case, one reaction (olein-stearin) appears to be accelerated more than the other. The scheme advanced in the preceding section may be made to give a satisfactory explanation; in that section the concentration of hydrogen at the catalyzing surface

Fig. 40*ff*.—Runs A & B.Fig. 40*gg*.—Runs C & D.Fig. 40*hh*.—Runs C & E.

was taken to be the controlling factor. Now increasing the percentage of catalyst must increase this concentration, for the average distance between a catalyst particle and the hydrogen bubble surfaces is made smaller, thereby decreasing the lag between the "demand" for hydrogen at the catalyst surface, and the "supply," which must be kept up by the processes of solution and diffusion. Thus an increase in percentage of catalyst would cause an increase in the formation of stearin relative to the change in linolin, as in the two curves reproduced above.

**Effect of Agitation.** The influence of degree of agitation on the path of hydrogenation was determined first by comparing Experiments *C* and *F* (Fig. 40*m*), in which an iron apparatus with mechanical agitator was used. "Degree of Agitation" is a magnitude which is not easily expressed in quantitative form, but the r.p.m. of an agitating device may serve as an index of the agitation, as least for moderate speeds.

Another pair of experiments carried out in the glass flask, bubbling hydrogen, conditions were identical in both experiments except that in Run *H*, the hydrogen was bubbled through the flask at approximately twice the rate used in Run *G* (Fig. 40*jj*).

In both pairs of experiments the influence of increased agitation is shown to be the same as that of increased pressure or per cent catalyst, and in the case of Runs *G* and *H* the variation in the curves is striking. The effect of doubling the volume of gas supplied, when the bubbling is already vigorous, may well be

to increase the true "agitation" many times. On the other hand, doubling the r.p.m. of a mechanical agitator possibly does not even double the agitation, since at high speeds there is a strong tendency for the whole body of oil to rotate without much disturbance.

It may readily be seen that the "mechanism" suggested in the preceding section applies to the present case just as well, since the effect of increasing the agitation is to increase the number and surface of hydrogen bubbles and also to decrease their average distance from catalyzer particles.

**Size of Apparatus.** The size of the apparatus in which the hydrogenation is carried out apparently does not affect the path of the hydrogenation as appears from the data of Runs *I* and *J* (Fig. 40*kk*). It is of course, not certain that 135 r.p.m. produces the same "degree of agitation" in both cases; if the agitation

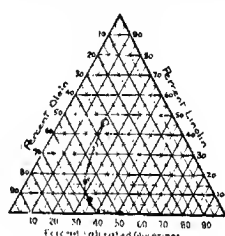
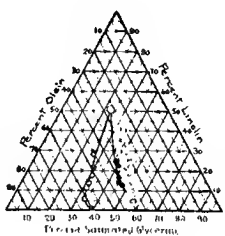
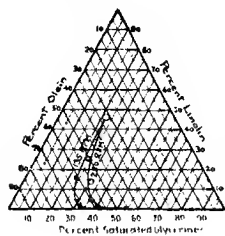


FIG. 40*ii*.—Runs C & F. FIG. 40*jj*.—Runs G & H. FIG. 40*kk*.—Runs I & J.

is really better at this speed in the large machine, the effect of the increase in size on the path of the hydrogenation is in the opposite direction to the effect of increased agitation.

#### INFLUENCE OF MATERIAL OF CATALYZER

When some other catalyst than nickel is used as in Experiment *K*, in which 1 per cent palladium (in  $\text{PdCl}_2$ , method of Paal patent\*) acted as catalyzer, the hydrogenation curve is found to have the same general characteristics as those described before. Bubbling apparatus was used, a temperature of  $135^\circ \text{C}$ . and atmospheric pressure. No experiment using nickel catalyzer is available to compare directly with it.

#### EXPERIMENT WITH PALLADIUM AS CATALYZER

Run Sample	IODINE NUMBER		PERCENTAGES CALCULATED.		
	Fat.	Liquid Fatty Acid	Saturated Glycerides.	Olein	Linolin.
Ko	108.4	142.8	20.6	33.5	45.9
1	89.1	125.0	25.5	46.0	28.5
2	76.6	113.1	29.2	52.8	18.0
3	64.5	97.1	30.6	63.8	5.6
4	53.0	90.3	38.6	61.3	0.1

\* Carl Paal, U. S. Patent No. 1,023,753, April 16, 1912. An equivalent amount of solid  $\text{Na}_2\text{CO}_3$  is used as a neutralizing agent.

## SUMMARY OF HYDROGENATION CURVES

To summarize the conclusions from the preceding experiments, it appears that the chemical character of a partially hydrogenated oil is determined by the conditions of the hydrogenation. Thus to obtain a product of the same iodine number as another but relatively higher in saturated glycerides and linolin, the operating conditions should compare as follows with those in the other case: temperature lower, pressure higher, agitation more violent and percentage catalyzer greater. It is interesting to note that it is possible to hydrogenate the linolin to olein with only the slightest increase in saturated glycerides by operating at a high temperature, low pressure and low agitation, and using only a small amount of catalyzer.

## II. CHANGES IN CHEMICAL CONSTANTS OF OIL DURING HYDROGENATION

Of all the "chemical constants" of cottonseed oil, the iodine number (with its variations, the "hydrogen number," Mummé number and heat of bromination), is the only one which is changed markedly by hydrogenation. Saponification value, acetyl value, Reichert-Meisels number and percentage of free fatty acids change either not at all, or only slightly.

The drop in iodine number, however, is one of the most striking effects of hydrogenation, and it has been commonly used in the past to indicate the progress of the reaction.\* Fokin concludes, from a study of the hydrogen absorption, that "the reduction procedure is included in the category of monomolecular reactions," but notices that the curves "often show a straightening out toward the abscissa axis." He comes to the conclusion that the conditions which determine the shape of the curve are: (a) the velocity of diffusion of the gas (presumably through the oil); (b) the condition of the catalyzing surface; and (c) the presence of catalyzer poisons. Very similar conclusions were published recently by Boeseken,† but most of his work was on organic compounds of lower molecular weight than the oils.

**Pressure.** Early investigators appreciated the fact that the hydrogenation reaction is accelerated by pressure, and Moore, Richter and Van Arsdell state that, so far as is known, all of the commercial oil-hardening processes are carried out at gas pressures ranging from 20 to 150 lb. or even higher. Comparison of the two curves of Fig. 4M shows that the time required to reduce the iodine number of the oil to any specified figure is roughly cut in half by doubling the pressure, i.e., in these experiments the rate of hydrogenation was approximately proportional to the hydrogen pressure.

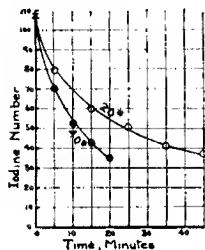
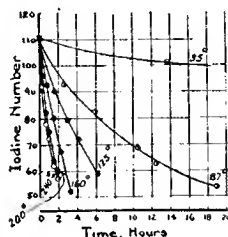
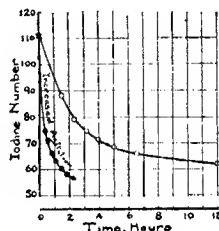
**Temperature.** It is likewise well known that the hydrogenation reactions in oil have a positive temperature coefficient, i.e., the rate is greater the higher the temperature, although the thermal decomposition of the oil sets an upper limit to the available range at about 250° C. The hydrogenation reactions in oil have a positive temperature coefficient in the range between 35° and somewhat above

\* Paal-Roth, Ber., 41, 2282-2291; Fokin, Z. angew. Chem., 22, 1451-9, 1492-1502; Bömer, Z. Nahr. Genussm., 24, 104-113.

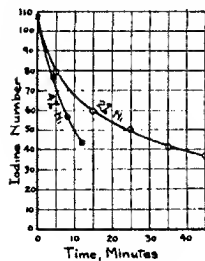
Paal and his co-workers, and Fokin recorded the volume of hydrogen absorbed at various stages of the process, thereby determining directly the amount of saturation which had taken place, instead of indirectly by means of the iodine number.

† Rec. trav. chim., XXXV, 1916, 260-287.

200° C.—possibly up to 240° C., but as may be seen from a study of the curves of Fig. 40*mm*, this coefficient drops consistently as the temperature rises. Thus for the range of temperatures 35° to 125° the time required to reach a certain iodine number is on the average decreased about 35 per cent for each 10° rise in temperature, while for the range 160° to 200° this coefficient is less than 20 per cent. Since the commercial processes nearly all operate at temperatures of 160° to 180°, it is evident that no material gain in time could be made by the use of higher temperatures, and the point of maximum economy is probably being realized.

Fig. 40*ll*Fig. 40*mm*.Fig. 40*nn*.

**Agitation.** The increase in velocity of reaction due to increased agitation of oil and catalyzer with hydrogen is shown in Fig. 40*nn*. In this case an increase of about 100 per cent in the volume of hydrogen supplied increased the velocity of the reaction 800 to 1000 per cent. In apparatus of this type handling charges of commercial size it is not usual to cause such violent agitation as is easily brought about in a 2-litre flask, and it is doubtful whether doubling the hydrogen supply would, on a large scale, more than double the reaction-rate. The importance of efficient agitation, or of intimate commixture of the oil, catalyzer and hydrogen, has apparently been realized by nearly all of the workers in this field, as witness the patent files, but there is no observation recording such a great increase in agitation as the above, brought about by such simple means.

Fig. 40*oo*.

**Catalyzer.** As in practically all catalytic reactions, the speed of hydrogenation is increased as the percentage of catalyzer is raised.

The time required to reach a given iodine number is roughly proportional to the percentage of catalyzer (Fig. 40*oo*). Considerations of outlay required for catalyzer preparation and recovery limit the amount used in commercial batch processes, however, to 1, or at most, 2 per cent. When a very good grade of

refined oil is used, as little as 0.1 per cent nickel is common practice, high pressure and agitation being relied upon to reduce the time consumed.

#### SUMMARY OF IODINE NUMBER-TIME CURVES

To summarize, increasing the pressure, temperature, agitation or amount of catalyzer will increase the rate at which cottonseed oil is hydrogenated. This

increase in rate is roughly proportional to the increase in pressure or amount of catalyzer, while raising the temperature  $10^{\circ}$  in the region of common practice,  $160^{\circ}$  to  $180^{\circ}$ , increases the rate only about 20 per cent. Increase in agitation (difficult to measure quantitatively) produces a marked increase in the reaction-rate.

### III. CHANGES IN PHYSICAL CONSTANTS OF OIL DURING HYDROGENATION

The most striking effect of the hydrogenation of an oil is, of course, the gradual increase in solidity, with the accompanying change in such physical constants as melting-point and titer.

**Melting-point.** Oil was hydrogenated with mechanical agitation of 108 r.p.m., temperature  $160^{\circ}$  C., pressure 20 lb., catalyzer 5 per cent. nickel on a carrier. The melting-point and iodine number were among the constants determined on each sample, and these constants compared as follows:

	$M_0$	$M_1$	$M_2$	$M_3$	$M_4$	$M_5$	$M_6$
Melting-point, $^{\circ}$ C . . . .	9.0	39.4	40.8	45.8	48.0	48.9	60.5
Iodine number. . . . .	107	74.3	66.7	61.0	54.5	48.5	0.4

There can be no doubt that while the two ends of this curve remain fixed, the intermediate points are capable of considerable variation from the curve, depending on the conditions of hydrogenation. We have, for instance, the points *A* and *B* on Fig. 40pp. Sample *A* was made by one of the "continuous" processes from the same kind of cotton-oil, while Sample *B* was made at a very high temperature.

**Titer.** The titer of an oil or fat, being the solidification-point of its fatty acids, might be expected to share the characteristic of the melting-point of the

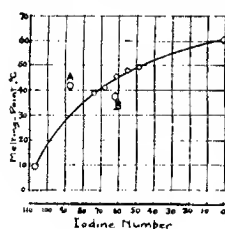


Fig. 40pp.

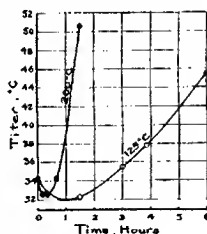


Fig. 40qq.

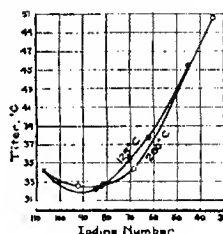


Fig. 40rr.

fat, namely, a gradual increase of hydrogenation. It is found, however, to show the peculiarity of first decreasing, passing through a minimum, and then increasing steadily. Cotton-oil was hydrogenated with 5 per cent of nickel, on a carrier, in one case at  $125^{\circ}$  C., and in the other at  $200^{\circ}$  C. Titer and iodine number were among the determinations made on each sample. In Fig. 40qq titer is plotted against time and in Fig. 40rr against iodine number.

The apparently anomalous fact that the addition of more saturated, higher melting acids at first lowers, instead of raising the solidification point is evidently due to the existence of a eutectic, or low melting mixture of the components. According as the path hydrogenation carries the composition close to or far from this point the minimum attained will be lower or higher. From Fig. 40rr

it is evident that the low-temperature run passed closer to the eutectic point than did the high-temperature run. Below iodine number 50 the two runs were practically identical, as would be expected from the fact that since linolin has largely disappeared the two hydrogenation curves of component glycerides cannot differ very greatly.

#### IV. RESPONSE TO HALPHEN TEST

Hydrogenated cottonseed oil was first stated by Paal and Roth \* to give no coloration when subjected to the characteristic Halphen test † and the same statement has been made by later investigators. The amount of hydrogenation which is required to render the oil just incapable of responding to the test was investigated by Moore, Richter and Van Arsdel. To determine that point a quantity of oil was hydrogenated at a temperature of 150° to 160° C., 2 per cent nickel on a carrier acting as catalyzer. Samples were taken (a) of the original oil, (b) of the mixed oil and catalyzer before heating, (c) of the mixed oil and catalyzer when heated to 150° C., five minutes being required to reach this temperature, (d) after three-minute hydrogenation, (e) after nine-minute hydrogenation, and (f) after fifteen-minute hydrogenation. A similar sample of oil was heated to 150° to 160° for twenty minutes in the absence of any hydrogen or catalyzer, and was then found to give the same intensity of Halphen test as Sample a. The other samples gave tests as follows:

Sample	Iodine Number.	Result
b . . . . .	104.9	Not noticeably diminished
c . . . . .	103.7	Distinctly weaker test
d . . . . .	102.7	Faint test in 3 minutes
e . . . . .	101.3	Faint test after heating 1½ hours
f . . . . .	97.6	Negative even after heating 1½ hours

A drop of four units in iodine number may be said to have destroyed the chromogenetic substance.

#### MISCELLANEOUS PUBLICATIONS ON HYDROGENATION

A paper by **Lessing** on Catalysis in the gas industry appears in *J. Gas Lighting*, 1914, 127, 570-573; see also *J. S. C. I.*, 1914, 1193. **Rivals** ‡ discusses the subject of oil hydrogenation quite fully. The hydrogenation of oils and fatty compounds is described by **Jaubert** § who gives an outline of the whole industry, including a discussion of catalysis, the production of hydrogen and the hydrogenation of fats, with a detailed description and drawings of processes used by a number of the largest concerns in the world. The same subject is discussed by **Ueno** who refers to the following subjects: hydrogenation

\* Paal and Roth, *Ber.*, 42, 1909, 1541-1553.

† *J. A. O. A. C.*, No. 3, II, 1916, 313.

‡ *Rev. gen. chem.*, 18, 9-26, 1915

§ *Rev. gen. chem.*, 18, 117-33, 141-60, 1915.

|| *J. Chem. Ind. Japan*, 8, 545-65, 1915; *Chem. Abs.*, 1916, 535.

tion of sardine oil on a semi-commercial scale; examination of the intermediate products of hydrogenation; durability of the activity of nickel and revivification of spent catalyzer; hydrogenation at low temperatures; and the relation of the catalytic activity of nickel-kieselguhr catalyzer to the proportions of the nickel and its carrier. A description of the **Wilbuschewitsch** apparatus and its manipulation for the manufacture of hardened oils and of catalyzers is given by **Schicht**.<sup>\*</sup> **Sjoquist**,<sup>†</sup> describes the Wilbuschewitsch process and some experiments made in the laboratory on the hardening of fats. The catalytic hardening of fats is discussed by **Siegmund**.<sup>‡</sup> An address given by **Hertzog** on the subject of fat hardening appears in the *Seifensieder Zeitung*, 43, 589. § A comprehensive account of the history of the hardening process, properties of hardened fats and their utilization for various technical purposes and for food is furnished by **Fahrion**. || The hydrogenation of fats is reviewed by **Redgrove**,<sup>¶</sup> and the review includes a discussion of the following topics: historical catalysts, apparatus, and uses. No new material is introduced, but the patent literature is largely drawn on. **Klimont**<sup>\*\*</sup> has published a paper on technical oil hardening apparatus. An interesting and useful summary of some of the more recent applications of catalysis, especially in inorganic chemistry, is published by **Jobling** in a book entitled "Catalysis and Its Industrial Applications," Blakiston's Son & Company, 1916. The book contains a brief chapter on hydrogenation and catalytic material used in carrying out hydrogenation processes. According to the *Journal of Industrial and Engineering Chemistry*, 1918, p. 158, the Tariff Commission of the United States, in making an inquiry in regard to chemical industries, proposes to study, as one subject, the development or invention in the United States or abroad of new or improved processes which are likely to influence the conditions of international competition; for example, the hydrogenation of fatty oils.

In a German patent application filed June 14, 1913, by the **Bremen Besigheimer Oelfabriken**, the claim is made for the transformation of drying oils such as soya bean oil, sunflower oil and linseed oil to

<sup>\*</sup> *Seifen. Ztg.*, 1914, 1189.

<sup>†</sup> *Deut. Parfum. Ztg.*, 1916, 7; *Seifen. Ztg.*, 1916, 234 and 257; *Chem. Zentr.*, 1916, I, 1206.

<sup>‡</sup> *Oesterr. Chem. Ztg.*, 1916, 19, 88.

§ See also *pharm. Post.* 49, 309; *Chem. Zentr.*, 1916, I, 1282, II, 776.

|| *Naturwsschn.* 4, 283-7; *Chem. Zentr.*, 1916, II, 285; *Chem. Abs.*, 1917, 2157; *Chem. Umschau*, 1916, 23, 155.

¶ *Chem. Trade J.*, 60, 273.

\*\* *Chem. Apparatur*, 1916, 3, Nos. 3 and 4; *Seifen. Ztg.*, 1916, 168.



non-drying oils by partial hydrogenation.\* Hydrogen is added until a sample tested with the refractometer shows that the oil has lost its drying properties. A careful review on the hydrogenation art is presented by **Bergius** together with certain figures as to cost of hydrogen and catalyzer, which are of interest.† **Ellis** has reviewed the progress of the industry in *Oil, Paint & Drug Reporter*, Oct. 26, 1914, p. 18. A paper by **Jaubert** on the hydrogenation of oils and fats appears in *Mémoires de la société des ingénieurs civils de France*, Vol. 67 (1915), No. 7-12, 305-353. In a review by **Fabris** of the fatty oil industry ‡ the subject of hardened or hydrogenated oils is discussed. *L'Industrie Chimique*, Apr., 1916, furnishes data on various oil hardening plants. Laboratory experiments on oleic acid vapor in a stream of hydrogen under reduced pressure, on liquid oleic acid and hydrogen under various pressures, and on the reduction of cottonseed oil by hydrogen under high pressures are reported by **Shaw**§ (see p. 26). To effect reaction between gases and liquids **Andersen** proposes the use of what he terms "porous metals" and their alloys as catalysts, such as iron, uranium, tungsten, etc. The walls of the vessel in which the reaction takes place may be coated with the porous material.|| **Robson**¶ reports that oils obtained from the waste lyes produced in the manufacture of sulphate pulp for paper-making are sent to England to be hydrogenated. Robson comments on the early history of hydrogenation of fatty oils, especially the Normann patent. The treatment of wool grease with hydrogen to improve its quality is proposed by **Ellis**.\*\* A method of adding the elements of water to unsaturated organic acids is advanced by **Schicht A. G.**, and **Grün** †† which consists in heating a salt of the acid, e.g., linolic acid under pressure, with water, in presence of a small quantity of an alkaline substance. In lieu of free hydrogen a body capable of liberating hydrogen on contact with a catalyzer is proposed by **Kayser** ‡‡ for hydrogenating fatty oils. Borneol is recommended for this purpose. **Boehringer** and **Soehne** §§ hydrogenate unsaturated

\* *Seifen. Zeitung*, 1915, No. 3, 51.

† *Zeit. f. angew. Chem.*, 1914, 525.

‡ *Chem. Abs.*, 1915, 2602; *Ann. chim. applicata*, 1915, 349.

§ *J. S. C. I.*, 1914, 771.

|| *J. S. C. I.*, 1913, 999, French Patent No. 457,569, May 7, 1913, English Patent No. 7,839, April 3, 1913, *Seifen. Ztg.*, 1914, 1174.

¶ *Drugs, Oils and Paints*, 1914, 211.

\*\* U. S. Patent No. 1,086,357, February 10, 1914.

†† German Patent No. 287,600, July 16, 1914; *J. S. C. I.*, 1916, 186.

‡‡ *J. S. C. I.*, 1915, 560; U. S. Patent No. 1,134,746, April 6, 1915.

§§ *Chem. Abs.*, 1916, 1080, 1780; British Patent No. 21,883, November 2, 1914; Swiss Patent No. 71,689, February 1, 1916.

substances in solution or suspension in water or alcohol, using a catalyst of the nickel group. In a Japanese patent issued to the **Hydroil Co., Ltd.**,\* unsaturated fatty acids, their glycerides, and other esters, are treated with hydrogen or hydrogen-containing gases in the presence of heated powdered metallic oxides, by means of which their saturated compounds are obtained. **Schmidt and Blaukenhorn**† propose to carry out catalytic hydrogenation by employing as the reducing gas, carbon monoxide admixed with water vapor. The process is recommended in connection with the reduction of nitrobenzene to aniline. **Barnitz**‡ observes that the consumption of hydrogen by fatty oils varies usually between 2870 and 4300 cu.ft. per ton. It has been stated § that 1 ton of oleic acid requires 2800 cu.ft. of hydrogen, while a like amount of triolein calls for 2680 cu.ft. of the gas. A process for solidifying fats, fatty oils, mineral waxes, or mineral oils and converting them into dry pulverulent products by means of malt extract or maltodextrin is described by **Hamburg**||. An apparatus for hardening oil is described by **Uchida**¶ and comprises the following elements: a container for the fats and oils, a supply pipe for hydrogen, a device for breaking up the current of hydrogen into bubbles, and discharge pipes for the waste gases.\*\* A pamphlet giving a brief survey of oil hardening has been published by **Fahriou**,†† *L'Industrie Chimique* (April, 1916) reviews the subject of oil hardening.

A process of hydrogenating oils which has been devised by **Walker** ‡‡ involves the use of a closed receptacle in which a body of oil to be hardened is placed. This oil contains finely-divided catalyst. The receptacle contains a shelf supporting a bed of catalyst which is placed above the body of the oil. The mixture of oil and finely-divided catalyst is pumped from the bottom of the receptacle to the top where it is sprayed upon the bed of the catalyst and passing there through collects in the body of oil beneath. The latter is stirred by an agitator while hydrogen is blown through the oil. The unabsorbed gas is withdrawn from the top of the receptacle and is passed through a condenser to remove moisture. It is then returned to the bottom of the receptacle. Thus both the oil and the gas are constantly circulated through the oil container. A compilation of patents of the United States, Great Britain and Germany, relating to the manufacture of butter substitutes, hydrogenated oils and milk products having substituted fats, has been prepared by **Mock & Blum**, patent lawyers, 220 Broadway, New York City.

\* No. 30,057, September 19, 1916.

† U. S. Patent No. 1,237,828, August 21, 1917.

‡ *Met. Chem. Eng.*, April 1, 1916.

§ *J. S. C. I.*, 1914, 1140.

|| French Patent No. 466,419, December 20, 1913; *J. S. C. I.*, 1914, 603. See also British Patent No. 29,481, 1912; *J. S. C. I.*, 1913, 672.

¶ Japanese Patent No. 31,304, July 12, 1917; *Chem. Abs.*, 1918, 234.

\*\* See also **Asahi Electrochemical Co.**, Japanese Patent No. 31,393, August 7, 1917; *Chem. Abs.*, 1918, 234.

†† *Die Härtung der Fette*, Braunschweig, 1915.

‡‡ U. S. Patent 1,276,290, August 20, 1918.

## CHAPTER IV

### CATALYZERS AND THEIR ROLE IN HYDROGENATION PROCESSES

#### THE BASE METALS AS CATALYZERS

Catalyzers, those bodies which modify reaction velocity without stoichiometrical participation in the reaction, are destined to find another important industrial application in the hardening of oils.\*

For present purposes a catalyzer may be simply, though less accurately, defined as a material or "exciter" which brings about a reaction between substances otherwise incapable of reacting, the catalyzer itself at the end of the reaction being unchanged. Thus fatty oil and hydrogen do not unite readily unless nickel or some other catalytic body is present to serve as a carrier or go-between to bring about the reaction.

The previous illustrations show the variety of methods proposed for mingling oil, hydrogen and catalyzer. Among these are several of excellent efficiency. But, after all, the virility, so to speak, of the process, depends on the *catalyzer*. With a powerful catalyzer the hydrogenation of oils becomes a rapid, simple procedure; almost, it sometimes seems, independent of the nature of the hydrogenating apparatus.

Catalyzers recognized as useful for the purpose are nickel and palladium, although platinum, copper, iron and other metals have been used to some extent. Nickel oxide, as stated, has been employed by Bedford and Ipatiew. Wimmer recommends organic salts of nickel, such as the formate, acetate or lactate.

As nickel is probably the most important of these catalyzers, in view of its efficiency and relatively low cost, it will be first considered.†

\* Abel. Zeitsch. f. Elektrochem. (1913), 933-951, gives a bibliography on catalysis. Conroy, J. S. C. I., 1902, 302, discusses the industrial side of catalysis. See also Jobling, Chem. World (1914), 17; Agulhon, J. Agr. tropicale (1913), 375; Stern on Catalysis, Fortschritte d. Chem. Phys. u. Phys. Chem. (1913), 249. A very good review of the subject of oil hardening and the catalyzers employed for the purpose is contributed by Meyerheim, Fortschritte d. Chem. Phys. u. Phys. Chem. (1913), 293. Another review appears in the Bulletin of the Imperial Institute (1913), 660.

† Nickel is recommended as the best catalyzer for hardening whale oil, Seifen. Ztg. (1913), 1412.

The preparation of an effective nickel catalyzer requires considerable care. The oxide or hydrate of nickel is first obtained by ignition of nickel nitrate, or precipitation of nickel hydrate from, say, a nickel sulfate solution by the addition of an alkali. Obtained in this or in any other suitable manner, the next step is the reduction to metallic nickel. For this purpose the nickel is placed in a receptacle which may be heated controllably, and hydrogen gas is passed over the mass at a temperature ranging from 250° to 500° C. or so, until water is no longer evolved.

The most sensitive catalyzers are obtained by reduction at the lowest possible temperatures. Nickel begins to reduce below 220° C., but at 270° C. the reduction is not complete even after long duration of exposure to hydrogen. A temperature of 300° to 350° C. gives fairly complete reduction and is a satisfactory working range. The lower the temperature at which the nickel is reduced, the more sensitive it is to various external influences, hence the preparation of this catalyzer should be conducted not only with respect to degree of activity, but also with respect to longevity.

Nickel is easily poisoned by chlorine and by sulfur in the sulfide form.\* The author has not experienced unfavorable results from the use of hydrogen gas passed through a wash bottle containing concentrated sulfuric acid and then conveyed directly to the catalyzer and oil. Traces of the acid were entrained by the gas, but the catalyzer remained in active condition during about two weeks usage under these conditions.

Copper is much less sensitive to poisons than nickel, but on the other hand it is much less active.†

Catalyzer made from the heavier forms of the oxide without supporting material, weight for weight, is hardly as efficient as when the active surface is increased by the use of a carrier. Hence we find many proposals for the production of catalyzers with a great diversity of carriers and extenders, ranging from pumice stone and kieselguhr to charcoal and sawdust.

\* The albumin contained in animal and vegetable fats and oils is a source of sulfur-containing gases (Bedford and Erdmann, *Jour. f. prakt. Chem.*, 1913, 426).

† Mailhe (*Rev. gen. sci.*, 24, 650) describes the scientific and technical uses of active nickel as catalyst in the reduction of organic compounds and in the hydrogenation of oils. He also discusses the catalytic properties of finely-divided copper and the commercial possibilities of metallic oxides (especially  $\text{ThO}_2$ ) as catalytic agents in processes requiring elimination of water (or water and hydrogen, depending on temperature) from organic compounds. Drawings are given, showing forms of apparatus. Much stress is laid on the maintenance of proper temperatures and on the use of pure hydrogen.

After reduction of nickel, as above, it should be kept out of contact with air as it is usually extremely pyrophoric and quickly loses much of its efficiency on exposure to the air.\* Consequently when treating oil with such a catalyzer, it is advisable to free the treating apparatus from air by flushing with hydrogen; also it is sometimes beneficial to heat the oil and bubble hydrogen through it for a short time prior to the introduction of the catalyzer.

The use of nickel as a contact body by Mond,† in 1888, is of historical interest in view of present developments. Mond found that if carbonic oxide or gaseous hydrocarbons be brought into contact with metallic nickel at a temperature of 350° to 400° C., or with metallic cobalt at 400° to 450° C., decomposition takes place into carbon and carbonic acid or hydrogen, the carbon combining with the metal. If now steam, at a moderate temperature, be introduced, this carbon combines with oxygen to produce carbonic acid, with simultaneous formation of free hydrogen. These various reactions take place simultaneously when the steam is passed through the apparatus along with the carbonic oxide or hydrocarbon, the ultimate products being carbonic acid and hydrogen. The former can be eliminated by any suitable means, such as by washing with milk of lime. The cobalt or nickel surfaces may be obtained by *impregnating pumice stone with a solution of the metal*, and reducing.‡

The Mond and Langer British Patent 12,608, of 1888, is entitled Improvements in Obtaining Hydrogen. From the specification the following is quoted:

"By the distillation or incomplete combustion in the presence or in the absence of steam, oil, lignite, wood, coke, animal carbon or organic substances in general, gases are obtained which consist chiefly of hydrogen, carburets of hydrogen, monoxide and dioxide of carbon and a greater or less quantity of nitrogen. The object of our invention is to eliminate from these gases the monoxide of carbon and the carburets of hydrogen, and at the same time to increase the amount of hydrogen contained.

"If a mixture of monoxide of carbon or carburet of hydrogen and steam be heated to white heat in the presence of firebricks or of oxide of iron, the latter is decomposed and the carbon of the gases is oxidized to carbon dioxide and the hydrogen set at liberty. The high temperature required for this reaction renders it of little profit and it is difficult to produce it on an industrial scale. We have found that if monoxide of carbon and hydrocarburets be placed in contact with metallic nickel or

\* Wimmer and Higgins (Seifen. Ztg. (1913), 556) prepare catalyzer by reducing the active material while it is enveloped in a protecting material, oil being recommended for this purpose.

† British Patent 12,608, Sept. 1, 1888.

‡ The use of nickel in the catalytic reduction of carbon monoxide to methane is set forth in U. S. Patents to Elworthy 738,303, Sept. 8, 1903; 777,848, Dec. 20, 1904; and 943,627, Dec. 14, 1909.

cobalt at a temperature not exceeding a red heat, these gases are decomposed into carbon and dioxide of carbon on the one hand and hydrogen on the other; the free carbon so formed placed in contact with steam at a moderate temperature decomposes the latter and forms dioxide of carbon and hydrogen.

"If the steam and the gases are mixed from the commencement, the two reactions take place simultaneously and the result is a gas practically free from monoxide of carbon and hydrocarbons. It is quite possible to attain our object by carrying out consecutively the two above-mentioned reactions and by repeating them continually with the same quantity of nickel and cobalt which will always be regenerated. We prefer, however, to carry out these two reactions simultaneously, at the same time employing the least possible amount of nickel and cobalt; with this object we spread the aforesaid metals on an indifferent refractory and porous material. For example, we saturate pieces of pumice stone with a solution of chloride of nickel or cobalt, dry and reduce at a higher temperature with hydrogen.

"In carrying out our invention industrially we lead the gases with an excess of steam into retorts or cylinders fixed in a suitable furnace and containing pieces of pumice stone impregnated with nickel or cobalt as above mentioned. When nickel is used, the reaction takes place at a temperature of 350° to 400° C. If cobalt be used, at a temperature of 400° to 450° C. The reactions which take place between the gas and the steam produce heat so that the given temperature once reached the reaction goes on of itself without need of external heating.

"It may, however, be advantageous to use gases or steam or both, heated to a suitable temperature before they are placed in the retorts. The gases so treated contain little or no monoxide of carbon. The carbonic acid can be separated in any known manner, such as by passing the gases through lime or caustic alkali.

"The foregoing process differs entirely from the plan of using an easily reduced oxide and oxidizing the carbonic oxide or hydrocarbons by means of that oxide at a bright red heat, as in our case no oxide is used, but a metal having but little affinity for oxygen, but a considerable affinity for carbon. The metal deprives the carbonic oxide of a part of its carbon and gives the latter up to the oxygen of the steam. This is done at a heat much below that at which oxide of iron or other like oxide would give up its oxygen."

Mond and Langer lay claim to the process of obtaining hydrogen by means of gases containing carbon monoxide with or without hydrocarbons which consists in treating such gases with metallic nickel or cobalt and with steam and separating from the hydrogen the carbonic acid resulting from such a treatment.

They also claim the use of pumice stone or other similar porous substance impregnated with one or more salts of cobalt or nickel so as to provide, when reduced, an extended metallic surface with only a small amount of actual metal.

These extracts are given because of the use by Mond and Langer, in 1888, of reduced nickel or cobalt on porous refractory material for catalytic purposes, although, to be sure, the object of the process was to produce hydrogen rather than to cause its combination with unsaturated bodies.

Carbon and hydrogen combine with difficulty, especially to form methane. At the ordinary pressure in the presence of nickel oxide, reduced nickel or a mixture of nickel and alumina, and up to 625° C., there is no formation of methane. Under great pressures its synthesis only occurs above 500° C. in the presence of the above substances or mixtures, and so much the better as the temperature becomes greater. In the presence of water and nickel, methane is decomposed at 500° C. into hydrogen and carbonic acid. The inverse reaction, i.e., reduction of carbonic acid to methane

in the presence of nickel and an excess of hydrogen at ordinary pressure, occurs at 450° C. Results are the same with nickel oxide. (Chem. Trade Jour., Oct. 25, 1913, 414.)

At ordinary pressure no methane is formed by combination of its elements in the presence of catalyzers such as nickel or nickel oxide, but under high pressures and at a temperature of 510° to 520° C., methane is formed. (Ipatiew Chem. Ztg. Rep. (1914), 15.)

Acetylene is converted into ethylene by treatment with hydrogen under pressure in the presence of catalyzers. The Elektro Chemische Werke G. m. b. H. (Zeitsch. f. angew. Chem. (1913), ref. 644) find that the production of ethylene from acetylene and hydrogen on a commercial scale is difficult, due to the gradual loss in the efficiency of the catalyzer. Even though the usual precautions are taken to remove the recognized poisons, such as hydrogen sulfide, sulfurous acid, chlorine and the like, there still remain in the gas certain impurities which cannot be eliminated by the usual absorption reagents. Accordingly it is recommended to wash the hydrogen with concentrated sulfuric acid, then to pass it over solid caustic soda, which treatment is said to remove the troublesome bodies. To effect the combination of the unaltered ethylene and hydrogen in the gaseous mixture resulting from the passage of these gases over a catalyst, the product is again passed over the catalyst under pressure. The reaction is stated to be quantitative and instantaneous. Nickel or a metal of the platinum group may be used as a catalyst. (German Patent 265,171, Oct. 16, 1912.)

From a very lengthy paper published by **Sabatier and Senderens** \* the following items on the preparation and use of catalyzers have been noted.

Access of air to the catalyzer oxidizes it and destroys or diminishes its activity. To prepare catalytic material one should use an oxide quite free of chlorine or sulfur. Good results are obtained by dissolving the metal in pure nitric acid and forming the oxide by calcination at a low red heat. Reduction of the oxide should be with pure hydrogen, free from chlorine or sulfur. Reduction should take place at a low temperature, always below a red heat, or the catalyzer will not be efficient.

Nickel reduced at a red heat has practically no activity. At 300° C. it gives a *very* active material if used *immediately*. It is better, however, to employ a temperature of 350° C. Copper is best treated at 300° C., while cobalt † requires 400° C. Iron is difficult to reduce. At 450° C. some 6 or 7 hours are required to completely transform the oxide into the metal. Nickel and copper are actually reduced near 200° C., so even if some oxidation of the catalyzer were taking place,

\* Ann. de Chim. et de Phys., 1905 (4), 319.

† The reduction of cobalt oxides by hydrogen and carbon monoxide at different temperatures is described by Kalnus. (Jour. Ind. Eng. Chem. (1914), 112-114.) For some metals the minimum temperature of reduction is lower with carbon mon-

because of the presence of oxygen in the hydrogen gas, immediate reduction would occur thereafter.

The hydrogen employed is dried with sulfuric acid, is then passed through a tube of Jena glass filled with copper turnings maintained at a low red heat and finally goes through a long tube filled with fragments of caustic potash.

The catalyzer should be prepared in the tube in which the material to be hydrogenated is treated.

For high temperatures a copper tube heated in a bath of equal parts of sodium and potassium nitrate (which melts at  $225^{\circ}\text{C}.$ ) may be used.

With regard to the life of the catalytic material the investigators state that there are three periods noticeable.

1. A short period when the catalyzer is becoming accustomed to the atmosphere of hydrogen and the body to be treated.

2. A period of normal activity.

3. A period of decline.\*

The second or normal period is generally very long, if no trace of bodies capable of altering the surface of the metal is present. For example, with a nickel catalyzer good results were secured for one month in the transformation of benzene into cyclohexane. The operation was interrupted each night and resumed the next morning. The slight oxidation over night did no harm as the oxide was reduced again the next day at the temperature of working, which was  $180^{\circ}\text{C}.$

If in the hydrogen there is a trace of certain bodies, the action of the catalyzer is rapidly suppressed. Even tiny traces of chlorine, bromine, iodine or sulfur paralyze the nickel. Nickel obtained from oxide carrying a little chlorine is usually devoid of activity. Nickel from oxide containing a trace of sulfur is likewise inefficient. The presence in the hydrogen of even faint traces of hydrochloric acid, hydrogen sulfide or selenium compounds produces the same disastrous effects. Traces of bromine in some phenol which was used paralyzed the nickel. The same thing happened with benzol containing this compound.

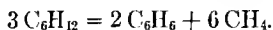
Catalyzers finally lose their efficiency either by traces of poisons or by a deposit of tarry or carbonaceous material on the catalyzer particles. On dissolving spent nickel in hydrochloric acid a fetid gas is evolved and brown carbonaceous material is deposited.

According to Sabatier and Senderens the operation should be conducted to prevent *liquid* coming into contact with catalyzer. The temperature limits practically are those imposed by maintaining the

\* These periods are similar to those noted in the case of ferments.



substance in a state of vapor. Too high temperatures sometimes cause decomposition. Benzene becomes cyclohexane at temperatures up to 240° C., but at 300° C. the cyclohexane gives benzene and methane:



Copper and platinum work well in case of ethylene groups, but are not satisfactory for hydrogenation of the aromatic ring. Nickel is effective on the latter.\*

Some peculiarities of catalytic nickel have been recorded by Senderens and Aboulenc.† These investigators state that the temperature at which nickel oxide is reduced by hydrogen is found to depend on the mode of preparation and treatment of the oxide used, there being also a considerable difference between the temperature at which reduction commences and that at which it is complete. Complete reduction is not effected below 300° C., but the mixture of metal and oxide thus obtained is more active than the metal prepared by total reduction at a higher temperature, the activity of reduced nickel being diminished by heating to a comparatively high temperature, although, at the same time, its catalytic properties are rendered more permanent. Pyrophoric nickel, when heated in the air, furnishes an oxide which is reducible at a comparatively low temperature, and reduced nickel of impaired activity may be restored, therefore, by oxidizing it and again reducing.

According to Moissan the protoxide of nickel in hydrogen at 230° to 240° C. blackens and reduces, giving a body pyrophoric at ordinary temperature. Muller states the protoxide of nickel at 210° to 214° C. in hydrogen loses 11 to 14 per cent of oxygen, apparently giving nickelous oxide which corresponds to a loss of 10.7 per cent oxygen. At 270° C. it passes into the metallic state. For hydrogenation the anhydrous or hydrated oxide of nickel supported on pumice is reduced at 270 to 280 degrees (Brunel); 280 degrees (Leroux); 255 to 260 degrees (Godchot); 245 to 250 degrees (Darzens).

Senderens and Aboulenc, however, after a protracted investigation, recorded results which in brief are as follows:

(a) Anhydrous nickel oxide: This oxide becomes green a little above 200° C. in presence of hydrogen, but the reduction commences only at about 300° C. and is slow at 330° C. It goes on much faster

\* Sabatier has reviewed the subject of catalytic action in organic chemistry, the publication appearing as Vol. III of the *Encycl. de Science Chimique applique aux arts industriels*.

† Bull. Soc. Chim. (1912), 11, 641.

at 380° C. up to two-thirds the amount of water which should be evolved. There reduction stops. To get complete reduction the temperature has to be raised to 420° C. The nickel obtained is pyrophoric. It serves very well for the hydrogenation of carbon monoxide, carbon dioxide, benzene and toluene, but does not work well with the phenols.

(b) Nickel oxide obtained by calcination: This shows a great resistance to reduction. It is necessary to raise the temperature to 420° C. to obtain two-thirds of the water of theory and to a red heat to secure complete reduction. Heated to this last-named temperature the product is inactive even with carbon monoxide which is very easily hydrogenated. It is pyrophoric, however. The efficiency of nickel as a catalyzer does not depend on any pyrophoric property. Non-pyrophoric nickel has been prepared which is a good catalyzer. Reduction of the oxide (b) at 420° C. gives about one-third oxide with two-thirds metal. This mixture is active and pyrophoric. It easily converts water gas into methane.

(c) Hydrate of nickel: Introducing hydrate, prepared in the laboratory, into the tube used for reduction, the dehydration was very slight at 200° C., while at 230° C. reduction took place and at 270° C. dehydration and reduction progressed, but rather slowly. In another experiment the same "hydrate" was reduced after gently heating in a crucible to remove the water. The reduction presented the same variations commencing about 230° C. and progressing very gently up to 270° C. at which point water was given off regularly for 6 hours in an amount corresponding to one-third the total expected from the reduction of the oxide. At 300° C. two-thirds of the water was collected and at 320° C. the remainder was obtained after treatment for several hours.

Another hydrate of nickel furnished by a chemical supply house was more difficult to reduce, not giving off as much water as the preceding at temperatures 20 to 30 degrees higher.

Oxides of pyrophoric nickel: These may be obtained by letting pyrophoric nickel oxidize in a thin layer in the cold or by heating. In the cold the oxidation is variable; when heated the reaction is complete in a moment. The oxides obtained in this manner commence to reduce at a temperature much lower than those from which the pyrophoric nickel was derived. For example, the oxide resulting from the simple exposure to the air of the pyrophoric nickel obtained from the hydrate (c) was reduced at 210° C. by hydrogen, giving about one-half the theoretic water.

The oxide obtained by moderate calcination in the air of this same

pyrophoric nickel takes up hydrogen at 250° C. giving off half the theoretic water; after which, to complete the reduction it is necessary to raise the temperature as in the preceding case.

The anhydrous oxide (a) commenced to reduce at 300° C., reduction was slow at 330° C. and normal only at 380° to 420° C. The pyrophoric metal which results when this material is heated in contact with air furnishes an oxide of which one-third is reduced at 280° C. and half at 320° C. The activity of the nickel reduced from these oxides is at least equal if not superior to that obtained by the reduction of the normal oxide.

When the nickel begins to weaken in catalytic effect it is necessary only to oxidize and then reduce it, in order to have the catalyzer completely regenerated.

Passivity of nickel as a catalyzer: If used to hydrogenate phenol for a day or two it will then hydrogenate cresol, but if used for a month on phenol it will not be active on cresol, although still active on phenol. By oxidizing and then reducing, the material is very active on cresol.

Anhydrous oxides and hydrates of nickel cannot be completely reduced to the metal at 300° C., but a mixture of the metal and oxide results. It is nevertheless true that such mixtures are more active than if complete reduction with corresponding elevation of the temperature had taken place.

Two stages of oxidation, derived from the same pyrophoric nickel of which in one case the reduction was arrested at 250° C. when one-half the oxide remained, and in the other case the material was heated up progressively to 350° C. to give total reduction, were tested. The latter hydrogenated xylene normally, while the former gave a hydrocarbon. To evade this destructive action in a number of cases the investigators heated the nickel after reduction to a higher temperature to diminish its activity and conserve its life as a catalyzer.\*

\* Padon and Fabris (J. S. C. I., 1908, 1083) showed that at ordinary pressure indene is not capable of combining with hydrogen in presence of reduced nickel at 300° C., but that at 250° C. two atoms of hydrogen are taken up. Ipatiew (J. Russ. Phys. Chem. Soc. (1913), 45, 994) finds that in presence of nickel oxide, indene unites with hydrogen at 250° to 260° C. and 110 atmospheres, yielding the hydrocarbon octahydroindene. The nature of the metal of which Ipatiew's high-pressure apparatus (J. S. C. I., 1911, 239) is constructed is found to exert an influence on the hydrogenation, in presence of cuprous oxide, of compounds containing ethylene linkages. Thus, in an iron tube, amylene (trimethylethylene) is readily converted into isopentane, while in a copper tube the reaction is incomplete, an equilibrium mixture of amylene, hydrogen and isopentane remaining:



in an iron tube and in absence of cupric oxide, no hydrogenation occurs. Similar

Several types of catalyzers have been proposed for oil hardening and in some cases processes have been prescribed for operation with specific catalyzers. From the standpoint of the support or carrier for the primary active material catalyzers may be divided into several well-defined groups, each exhibiting characteristic properties. The classification embraces:

#### CLASSIFICATION OF CATALYZERS

##### *Group A*

- I. Carrier porous, inert and coated but is not impregnated with catalytic metal.
- II. Carrier active, serving as a secondary catalyzer or feeder, is coated but not impregnated with catalytic metal.

##### *Group B*

- I. Carrier non-porous, inert and is fairly evenly coated with catalytic metal.
- II. Carrier non-porous, inert and instead of being coated is punctated with metal nodules.
- III. Carrier non-porous, active and is fairly evenly coated with catalytic metal.
- IV. Carrier non-porous, active, serving as a secondary catalyzer or feeder and instead of being evenly coated is punctated with metal nodules.

##### *Group C*

- I. Carrier porous, inert and is impregnated with catalytic metal.
- II. Carrier porous, active, serving as a secondary catalyzer and is impregnated with catalytic metal.

Other subdivisions follow if the catalytic material is used in a coarse condition or in a finely-divided state, etc. Superficially treated or coated carriers are regarded as more desirable for treating liquids, while the porous impregnated varieties find a better field of utility in the hydrogenation of gases or vapors which in admixture with hydrogen are capable of penetrating porous bodies into which viscous liquid compounds would not readily diffuse.

results are obtained with hydro-aromatic compounds. Further, hydrogenation in an apparatus of phosphor bronze in presence of reduced copper results in the establishment of an equilibrium, while, if iron turnings are also present, hydrogenation proceeds to an end. The slight catalytic activity of reduced copper in copper tubes may be regarded as due to poisoning of the catalyst; or the use of cupric oxide in iron tubes may result in a conjugated catalytic action.

Ipatiew (Chem. Centralbl. (1906), II, 87) found alumina to act as a dehydrogenating catalyzer on various bodies.

## CHAPTER V

### THE BASE METALS AS CATALYZERS

#### NICKEL CATALYZERS — Continued

Nickel oxide catalyzer is recommended by Bedford and Erdmann\* as preferable to the metallic forms and some of the features claimed for this material are noted in the following: They indicate that the hydrogenation of oils by means of finely-divided nickel, although now worked on a commercial scale, has the disadvantage that the catalyst



FIG. 41. — Photo-micrograph of a particle of crushed glass coated with nickel oxide (equivalent to 10 per cent of metallic nickel).

is extremely sensitive to small quantities of air and to traces of chlorine and sulfur compounds, which latter may be developed from protein, always present in vegetable and animal oils. Oxides of nickel are capable of acting as hydrogen carriers for the hydrogenation of oils at atmospheric pressure, and possess the advantage over metallic nickel of being relatively insensitive to gases containing oxygen and sulfur compounds; moreover hydrogenation proceeds with much greater velocity than with metallic nickel. Any one of the oxides of nickel may be used, viz., nickel sesquioxide, nickel monoxide or nickel sub-

\* J. Prakt. Chem. (1913), 87, 425.

oxide;\* with the sesquioxide and monoxide a temperature of about 250° C. is required, but with nickel suboxide 180° to 200° C. is sufficient. When the higher oxides of nickel are used they become partially reduced to the suboxide which is said to form a colloidal suspension in the oil. Hence a nickel oxide catalyst becomes more active after it has been used, owing to the formation of the suboxide. No reduction to metallic nickel occurs during the hydrogenation process, although in absence of oil, reduction of nickel oxides to metallic nickel by hydrogen takes place at 190° C. Nickel suboxide may be distinguished from metallic nickel by its lack of electric conductivity and by its inability to form nickel carbonyl when treated with carbon monoxide under pressure at a moderate temperature. Other metallic oxides (e.g., copper oxide, ferrous oxide) are also capable of acting as catalyzers in the hydrogenation of oils, but do not act so well as nickel oxide. The activity of nickel oxide is increased by small quantities of the oxides of aluminium, silver, zirconium, titanium, cerium, lanthanum and magnesium. Nickel salts of organic acids do not act as catalysts, but in presence of the heated oil are decomposed by hydrogen, yielding nickel oxides and, under certain conditions, also metallic nickel; the resultant nickel material then acts as a catalyst. Nickel formate in the presence of the heated oil is reduced by hydrogen to nickel suboxide at 210° C., while at 250° C. metallic nickel is also produced. In carrying out the hydrogenation, the oil is placed in a cylindrical copper vessel fitted with an agitator, and heated in an oil bath to 180° C. while a slow current of hydrogen is passed through. A small quantity of nickel oxide is then added, the temperature is raised to 255° to 260° C., a further addition of the catalyst is made and the supply of hydrogen is increased. The hydrogenation is controlled by examining test-samples of the oil as to melting point and iodine value. The oil becomes black possibly owing to the formation of "col-



FIG. 42.—Photo-micrograph of a particle of crushed glass coated with 10 per cent of reduced nickel.

\* Compare Moore, Chem. News (1895), 7182. Böhm (Seifen. Ztg. (1912), 1044) briefly discusses oxide catalyzers. See also Soap Gazette and Perfumer, 1913, 107.

loldal" nickel suboxide, which passes through a filter-paper, but can be removed by centrifuging. Nickel soaps are formed only to a slight extent, and probably in consequence of a secondary reaction during the cooling. The hydrogenized fat is free from hydroxy-acids. The catalyst after use contains some organic matter apparently composed partly of nickel palmitate or stearate, and other substances, one of which probably is nickel carbide. The process is easy to control if pure hydrogen is available, and in an experimental plant of 1 ton capacity Bedford and Erdmann report that more than 100 tons of different oils have been hardened by hydrogenation in the manner described.

Nickel oxide catalyzers have been made the subject of a number of patents.

English Patent 4702, of 1912, to Boberg and the *Techno-Chemical Laboratories, Ltd.*, London, proposes to prepare catalyzer through the reduction of a metallic compound such, for example, as ignited nickel carbonate, the reduction taking place with hydrogen under such conditions that the nickel contains one or more suboxides, or when nickel is employed a compound is formed which contains less oxygen than the ordinary oxide  $\text{NiO}$ .\*

The observation is made that in the reduction of ignited nickel carbonate by hydrogen the product obtained is just so much more efficient catalytically the lower the temperature at which the reduction takes place, because of the suboxide formed. The catalyzer apparently also contains some hydrogen. The preparation of the catalyzer is carried out by passing ignited nickel carbonate, free from injurious impurities, continuously in a slow stream through an inclined rotary cylinder, which is heated in part or throughout its length, while hydrogen is allowed to flow through in an opposite direction. By suitable regulation of the influx of the material as well as the proper regulation of the temperature, the reduction may be carried out in such a manner that one obtains a catalyzer which is partly or mainly composed of the suboxide. The most suitable temperature is between  $230^{\circ}$  to  $270^{\circ}$  C. and the length of the heating operation must be just so much more prolonged the lower the maintained temperature. Unnecessarily long heating must be avoided otherwise the reduction goes too far which causes a diminution in catalytic activity. The catalyzer so obtained can be used immediately for oil hardening or it may be pre-

\* The proposal by Boberg to prepare a catalyzer from nickel carbonate by ignition and reduction to form a mixture of nickel and its suboxide is criticized by the editor of the *Chemiker Zeitung* (*Chem. Ztg.* (1913), 481) as offering nothing novel in view of Bedford's disclosures in English Patent 29,612, 1910.

served in contact with air where it oxidizes very slowly, provided local over-heating is avoided.

One can also collect the catalyzer in water, filter and dry in the air; or it can be collected in an atmosphere of hydrogen which is gradually displaced by air.

The production of suboxide catalysts is also carried out by reducing nickel oxide as completely as possible and then controllably oxidizing the product in any suitable way as with air or oxygen diluted with an indifferent gas, such as carbon dioxide, so that the introduction of oxygen can progress without local overheating. Such oxidation can go on between 300° to 600° C.

The degree of catalytic activity of a metal oxide depends not only on its chemical but also on its physical properties. It is known that metal catalyzers, such as nickel, cobalt and iron, require very fine division for effective action. The same is also true of the oxides of these metals. The German Patent to **Erdmann and Bedford** (260,009, 1911) relates to oxide catalyzers in a voluminous form. The patentees state that metal oxides may be obtained in the form of an especially finely-divided voluminous material if one takes a concentrated aqueous solution of the nitric acid salt from which the oxide is to be made, mixes with it a water-soluble organic compound rich in carbon and then subjects the mixture to combustion by allowing it to fall, drop by drop, into a heated vessel. The strong evolution of gas which thus takes place, due to the combustion of the organic compound and simultaneous decomposition of the nitrate, produces nickel oxide in a very voluminous form. Especially recommended for this purpose are the sugars and carbohydrates, for these when heated by themselves produce a strongly-swelling carbonaceous mass.\*

As an example Erdmann and Bedford state that nitric acid of 1.42 specific gravity is diluted with an equal volume of water. Pure metallic nickel is introduced. After the reaction is complete the solution is heated for two hours with an excess of nickel in order to completely neutralize the nitric acid and to separate any iron present as a precipitate of iron hydroxide. The clarified nickel nitrate solution is evaporated to specific gravity of 1.6 and to one liter of this fluid, corresponding to 250 grams of nickel, 180 grams of powdered cane sugar are introduced. This solution is allowed to run in portions into a muffle heated to a low red heat. Each portion is heated until no

\* The use of sugar or gum in a somewhat similar manner has been described by Schroeder (J. S. C. I., 1902, 344 and British Patent 10,412, 1901), who found it possible to increase the porosity of catalytic material by ignition with such carbonaceous matter, so as to form blowholes or bubbles in the catalytic mass.



more red vapors depart, when the voluminous nickel oxide which is formed is removed from the muffle and a fresh portion of the solution is introduced.

In place of cane sugar other varieties of sugar may be applied and also water-soluble starch, dextrine, gum, tartaric acid or other water-soluble organic acid substances which are rich in carbon.

In a similar manner the oxides of cobalt and iron or other catalytically-active oxides may be brought into a voluminous form.\*

It is the belief of Erdmann † that the oxide catalysts are superior to metal catalytic material, because the former not only have strongly marked catalytic properties but they are more stable than the latter. Erdmann refers to prior investigations of Ipatiew who worked with various organic compounds other than fats, employing nickel oxide and hydrogen under very high pressure; while in the present case fatty material, it is claimed by Erdmann, is smoothly hydrogenated under ordinary atmospheric pressure. For example, linseed oil or any other fatty oil may be heated with one-half to one per cent of nickel oxide, such, for example, as may be obtained by calcining pure nickel nitrate at a low red heat. The temperature of the linseed oil is raised to about 255 degrees and a stream of hydrogen is passed through the oil when it is observed that the nickel oxide and oil mixture becomes deep black and the oxide appears to undergo subdivision and possibly transformation into a colloidal state, the solvent acquiring an ink-like appearance. At the same time hydrogen is absorbed and the oil is hydrogenated.

This "colloidal" form of nickel oxide catalyzer, which apparently has not been observed with metallic nickel, is regarded by Erdmann as of great importance in this art because it enables a finely-divided catalyzer of an effective nature to be so easily prepared. When the hardening process is finished the nickel oxide catalyzer clots and collects so that it may be separated readily from the hardened fat.

The analyses of the hardened products of linseed, peanut and sesame oil show that by the process an approximately pure glyceride of stearic acid is produced without any trace of oxy fatty acid impurity.

Nickel soaps form in the presence of free fatty acid only in an inconsequential way to an amount of about  $\frac{1}{100}$  of 1 per cent or so. This slight amount is said to remain along with the catalyzer in an undissolved state.

\* Suboxide of nickel is prepared for catalytic purposes, according to Bedford and Williams (J. S. C. I., 1914, 324), by heating a mixture of nickel oxide or an organic salt of nickel with oil in a current of hydrogen.

† Seifen. Ztg. (1913), 605.

The whole hardening process, when pure hydrogen is at one's disposal, is so simple with reference to the apparatus required, and operates so smoothly that the shifting from the laboratory experiments to work on a large scale is stated to have offered no difficulties.

In one experiment carried out by *Bedford and Erdmann* \* 3 grams of freshly prepared nickel oxide were added to 30 grams of cottonseed oil and treated with hydrogen at 260° C. until the oxide had become black in color and very finely divided. The solidifying point of the fat was then 48° C. The mixture was cooled to 185° C., 270 cc. of cottonseed oil added and a strong current of hydrogen passed through the oil and catalyzer (maintained at 185° C.), for one hour when the solidifying point was found to be 45° C.

Another interesting question to which reference has already been made is whether or not nickel oxide in oil is reduced to metallic nickel by hydrogen, and whether any finely-divided metal which might arise in this manner is a carrier of hydrogen.†

While nickel oxide ( $\text{NiO}$  or  $\text{Ni}_2\text{O}_3$ ) yields nickel in an hydrogen atmosphere at 260 degrees and even in fact as low as 190 degrees, the behavior of these bodies, according to *Erdmann*, is very different when they are immersed in oil. In the latter case the oil acts as a protective element and hinders or prevents complete reduction. The reduction goes no further than the suboxide stage, and *Erdmann* believes that some sort of an addition compound is formed with the unsaturated oil. If the catalyzer is removed from the hardened fat and entirely freed from the latter by extraction with benzol, the used catalytic material is obtained in the form of a soft black powder which is more or less strongly magnetic, but which does not possess any conducting power for electricity.

A great number of analyses have shown that the nickel content lies between nickalous oxide and a form of suboxide described by *Moore*.‡ Not the slightest trace of metallic nickel is found in the used catalyzer if the fatty oil is free from strongly reducing substances such as aldehydes or formic acid.

\* *Jour. f. prakt. Chem.*, 1913, 446.

† The possibility of nickel oxide and carbonate becoming reduced during hydrogenation operation, so as to actually yield a metallic catalyzer similar to that covered by the *Leprince and Siveke* basic patent, is considered by *Mayer* (*Seifen. Ztg.* (1913), 1224) who also discusses the situation in Germany respecting patented processes of hydrogenation.

Professor *Erdmann* (*Seifen. Ztg.* (1913), 1325) discusses the scope of the *Leprince and Siveke* German Patent 141,029 corresponding to the *Normann* British Patent 1515, 1903, especially with regard to the use of nickel oxide catalyzer in the form employed by *Bedford and Erdmann*.

‡ *Chem. News*, 71, 82.

The absence of metallic nickel\* is rather definitely shown through the indifferent electrical conductivity of some used nickel oxide catalyzer from which the fat had been removed, the oxide being pressed into block form for the purposes of such test. A control test made with catalyzer which before use had received an addition of a few per cent of freshly-reduced nickel showed, under like circumstances, a relatively high electrical conductivity. Also the very different behavior of carbon monoxide toward metallic nickel and nickel oxide indicates the non-metallic nature of the used nickel oxide catalyzer.

So in two ways it is alleged to have been shown that under normal conditions of the process of hydrogenation, nickel oxide is not reduced to metallic nickel. According to Erdmann, after numerous comparative tests, a great advantage of the process over those made known up to this time has been established. The fact that nickel oxide catalyzers experience a partial reduction to nickel suboxide brings up the question as to whether or not the suboxide is the only oxide of nickel which is capable of transferring hydrogen to unsaturated compounds.

In the application of the higher oxide the first phase of the hydrogenation which takes place at 250 degrees is that of the formation of magnetic suboxide, and the once-used nickel oxide catalyzer possesses more marked activity than the unused. With such a once-used catalyzer hydrogenation progresses with much greater rapidity and also at an essentially lower temperature. After use eight times the nickel oxide catalyzer was still active.

Erdmann prepared Moore's suboxide through electrical reduction from a solution of nickel potassium cyanide. This he found possessed the properties stated by Moore, namely, it was magnetic, reduced nitric acid, developed hydrogen with mineral acids and showed no electrical conductivity. The compound, both in water and in oil, showed colloidal properties. When introduced into hot cottonseed oil it distributed itself through the oil in the form of a very fine suspension which colored the oil black, and treatment with hydrogen at 210° C. indicated that the compound even at that relatively low temperature was an excellent reduction catalyzer.

In passing, it may be mentioned that other oxides besides nickel have been found to possess the property of transferring hydrogen.

\* Meigen and Bartels (*J. prakt. Chem.*, 1914, 301) consider the views of Erdmann, regarding the formation of nickel suboxide when employing an oxide catalyzer, to be untenable, and conclude that metallic nickel is formed under the conditions established by hydrogenation. Experimental studies in support of this position are detailed. From the analytical results, the electrical conductivity and the observed formation of nickel carbonyl, Meigen and Bartels consider metallic nickel to be indicated, contrary to the views of Erdmann.

This has been noted with copper and iron oxide. Osmium tetroxide has been found by Lehmann to effect hydrogenation while in itself becoming converted into colloidal osmium dioxide.

A comparison has been made by Erdmann between oxide catalyzers and organic-salt catalyzers, such as the formate, acetate, oleate and other similar salts which have been studied in connection with oil hardening, and Erdmann has reached the conclusion that these salts do not act directly as catalyzers. In order to effect hardening it is necessary to break down the organic salt. It does not in itself possess the property of acting as a hydrogen carrier. So long as it remains unchanged no hydrogenation takes place. As soon, however, as a sufficiently high temperature is reached, Erdmann thinks these organic nickel salts, under the influence of hydrogen, are decomposed in such a way as to form nickel oxide and the suboxide, which latter possesses the property of forming an oil colloid and becomes active as a catalyst.

Under some circumstances a mirror of metallic nickel forms on the walls of the vessel; this occurs especially easily when nickel oleate is used, and also has been noted with nickel formate when the oil is maintained at a relatively high temperature, approximately 250° C. The metallic nickel which forms as a mirror or otherwise, it is claimed, does not exert a catalytic action, but the nickel oxides which arise and which pass into the oil in a finely-divided condition are effective catalysts.\*

The application of organic nickel salts, such as nickel formate, suffers the disadvantage that the action is not immediate, because time is required to effect the decomposition of the formate. Furthermore, there is the loss in formic acid and the costliness of regenerating the catalyzer.\*

\* Bohm (Seifen. Ztg. (1912), 737, Soap Gazette and Perfumer, 1913, 107) advances the rather sweeping view that many of the patents issued subsequent to the Leprince and Siveke German Patent 141,029, 1902, have little or no standing. He states that operations involving changes in air pressure are common expedients of organic chemistry; that spraying oils to secure intimate contact with gases is well known, citing such use in the linseed oil industry; and that metallic catalyzers in the colloidal form may fall within the definition of a finely-divided metal. He, however, regards the metal salt catalyzers as being independent of the Leprince and Siveke Patent, but expresses some doubt as to the continuance of their use in Germany after the expiration in 1917 of German Patent 141,029.

The views of Bohm are criticized in the Seifensieder Zeitung (1912), 1001, his idea that almost all patents for oil hardening will lose their value with the expiration of the Leprince and Siveke Patent in 1917 being regarded as erroneous. The contrary is more likely to take place, that is, the value of these processes will advance. It is a matter of surprise that Bohm regards the metal salt catalyzers as independent of the Leprince and Siveke Patent. Nickel formate, as well as other salts, such as

Sabatier and Espil have studied the reduction by hydrogen of nickel oxide obtained by igniting the nitrate. Reduction takes place at  $170^{\circ}\text{C}.$ , at which temperature, after 112 hours, 72 per cent were reduced. Thereafter the reaction progressed more slowly and after 160 hours the conversion amounted only to 80 per cent. These and other observations appear to disprove the claim made by Glaser that below  $330^{\circ}\text{C}.$  not over 50 per cent of nickel are reduced and that the oxide  $\text{Ni}_2\text{O}$  is produced. In fact, the work of Sabatier and Espil would indicate the existence of a difficultly oxidizable oxide having the formula  $\text{Ni}_4\text{O}^*$ .

Sabatier and Espil in a further investigation of the question of degree of reduction of nickel oxide when heated in the presence of hydrogen make note† that a careful calcination of nickel nitrate affords nickel oxide which reduces to metallic nickel at a temperature of  $155^{\circ}\text{C}.$  without the production of a non-reducible suboxide. When the oxide is calcined at a bright red heat reduction takes place at  $155^{\circ}\text{C}.$ , but the action is slower.

An additional contribution to this subject by Sabatier and Espil (Comp. rend. 1914, 668) indicates that sufficient metallic nickel is formed from the oxide in oil to explain the catalysis observed in the case of the Bedford-Erdmann process. Sabatier and Espil use the term *coefficient of reduction* to represent the proportion of oxide reduced per hundred parts. At  $240^{\circ}\text{C}.$  on three hours exposure to hydrogen, an oxide of nickel which had been prepared by calcination at  $550^{\circ}\text{C}.$

nickel lactate, acetate, etc., proposed by Wimmer and Higgins, are first broken down into nickel oxide and acid; while under the influence of heat and hydrogen the organic acid is further decomposed and the nickel oxide, at least in part, apparently is reduced to metallic nickel. Without the presence of metallic nickel hydrogenation is thought to be scarcely possible.

The decomposition of nickel formate into acid and metallic nickel is said to be very easily demonstrated by a laboratory test. Wimmer and Higgins may perhaps conduct the process so as not to form metallic nickel. A serious disadvantage exists in the regeneration of the once-used contact material of this character; for reconversion into nickel formate, acetate and other costly organic salts is an expensive operation. The oxide catalysts likewise would be expected to form metallic nickel during the hydrogenation process, even though the reduction be only partial. From the work of Ipatiew such reduction apparently does not take place. Possibly the envelopment of the molecules of oxide by oil hinders the reducing action of the hydrogen.

The doubts formerly had with regard to the effectiveness of oxide catalysts have now vanished, for during a considerable period this contact material has been used for hardening oils on the large scale. A reduction of the oxides to the metallic state has not been observed under these circumstances.

\* Chem. Ztg. (1913), 1121.

† Chem. Ztg. (1913), 1549.

showed a coefficient of reduction of 93, while oxide which had been ignited at a bright red heat exhibited a coefficient of 32.8. (These figures relate to the dry oxide not in oil.) At 155° C. on 96 hours exposure to hydrogen, a light oxide gave a reduction coefficient of 56 and a calcined oxide was found to have a coefficient of only 2.5. The rate of reduction was found to be somewhat accelerated by increase in the rate of flow of hydrogen over the oxide mass. At 240° C., with a rate of flow of hydrogen of 6 cu. cm. per minute the coefficient was 44.5, at 17 cu. cm. the coefficient increased to 65 and at 24 cu. cm. the coefficient became 77.5. Sabatier and Espil note that elevation of the temperature greatly increases the speed of reduction. At 220° C. with oxide of nickel, the following coefficients were obtained.

1 hour.....	14.9
4 hours.....	57.6
5.5 hours.....	77.4
6.5 hours.....	78.0
7.5 hours.....	79.9
22 hours.....	99.6

At 250° C. the coefficients were found to be as follows:

$\frac{1}{2}$ hour.....	30.0
1 hour.....	52.0
1.5 hours.....	78.9
2 hours.....	87.0
2.5 hours.....	92.5
3 hours.....	95.3
15 hours.....	100.0

Between 190° to 240° C. the speed of reduction is an exponential function of the temperature. The reduction of nickel oxide at 175° C. gave a coefficient of 10 and on treating this product with carbon monoxide at 50° C. nickel carbonyl was obtained. Sabatier and Espil conclude that a suboxide is formed by reduction in this manner, having the composition  $\text{Ni}_4\text{O}$ , corresponding to the coefficient 75. This suboxide is not, however, irreducible but is, as stated above, more slowly reduced than the protoxide.

Dry hydrogen has been found to reduce the oxide better than moist gas and in practice it is recommended that the hydrogen employed for reduction purposes be freed from moisture before use.\*

† Sabatier and Espil have observed that moist hydrogen is at least as active as dry hydrogen in the hydrogenation of benzene and phenol (Bull. Soc. Chim., 1914, 228).

The rate of hardening of cottonseed oil by nickel and nickel oxide catalyzers has been investigated by **Meigen and Bartels** (J. prakt. Chem., 1914, 293) and their results are shown in Fig. 43. Curves 1, 2 and 3 were derived with metallic nickel at 170° C., and 4 and 5 with nickel oxide at 250° to 255° C. The amount of catalyzer in all cases corresponded to two per cent of nickel oxide. No. 1 was obtained with nickel prepared from the carbonate, No. 2 from reduced oxide and No. 3 from a commercially-used catalyzer. The oxide employed in Nos. 4 and 5 was obtained by ignition of the nitrate. These curves indicate a slower action for the oxide, which Meigen and Bartels attribute to the time required for preliminary reduction of the oxide after its addition to the oil, and before actual hydrogenation of the oil occurs.

Free oleic acid can be hardened very easily by means of a nickel oxide catalyzer, according to *Bedford and Erdmann*.<sup>\*</sup> Nickel oleate forms only in slight amount.

Pure nickel, obtained by reduction of the nitrate, according to Chem. Fabr. auf Actien,<sup>†</sup> is inactive for the purpose of converting

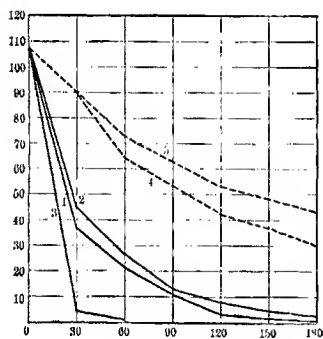


FIG. 43.

borneol into camphor; if, however, a small quantity of sodium carbonate be added to the nitrate before reduction, a very active product is obtained; a similar mixture is obtained by adding 0.17 per cent of pure sodium oxide to the nickel; other bases or salts which are not readily reduced at a red heat may be used in place of sodium oxide. Further, if a small quantity of certain other metals is introduced into the nickel, the mixture will have a very powerful catalytic action.

Mixtures of 6.7 per cent of cobalt or copper with 93.3 per cent of nickel may be used; they are obtained by the reduction of the mixed nitrates. The process is not confined to the use of nickel; it is stated that other metals possessing catalytic action can be used with equal effect.

By a method somewhat similar to that of *Bedford and Erdmann* the proposal comes from **Kast** <sup>‡</sup> to prepare catalysts in a finely-divided volu-

<sup>\*</sup> Jour. f. prakt. Chem., 1913, 450.

<sup>†</sup> French Patent 401,876, April 8, 1909; German Patents 219,043 and 219,044, 1908.

<sup>‡</sup> U. S. Patent 1,070,138, Aug. 12, 1912.

minous condition by heating the trinitrophenol salt of a heavy metal. These salts are combustible and when ignited they expand greatly, so the resulting ashes (metal or metal oxide) are found to be in a voluminous, spongy form. Kast claims that the usual procedure of precipitating a salt solution (with or without a carrier) yields a coarse crystalline precipitate, and that reduction by heating in a reducing gas slags the precipitate in consequence of which the catalytic effectiveness is considerably diminished. To avoid danger of an explosion when decomposing the trinitrophenol compound by ignition Kast adds oil or tar as a diluent. He also recommends for this purpose nitrate of ammonia, as this salt evolves large quantities of gas on heating and leaves no residue. The formation of slag which Kast objects to in ordinary reduction seemingly would be aggravated when a salt of trinitrophenol is burned under these conditions.

The hydrogenation of unsaturated fatty acids and their esters may be effected, according to **deKadt**,\* by means of hydrogen in the presence of a catalyst consisting of a soap of a heavy metal or of a noble metal, made from a fat or fatty acid having a melting point higher than that of the saturated compound to be produced. For example, the nickel soap, or preferably a mixture of the nickel and iron or copper soaps of the fatty acids of stearine or Japan wax, is dried and powdered, and can then be intimately mixed with the oil to be hydrogenated. After hydrogenation the oil is left quiescent at a temperature above its melting point, when the soap particles will agglomerate and settle on cooling. If, however, the oil is kept in motion and filtered, the soap does not pass through the filter. It is stated that this process is more efficient than when metallic catalysts are used, owing to the more intimate contact between the catalyst and oil or fat which is here obtained.

Basic compounds of high molecular fatty acids with certain of the heavy metals are proposed as catalyzer formative material by **Hausmann**.† The compounds dissolve in the oil undergoing treatment and in the presence of hydrogen afford active catalytic bodies. The temperatures employed range from 100° to 180° C. After the oil has been hardened it may be treated with dilute acid to remove the catalyzer.‡

The employment of a basic salt of a heavy metal (nickel or copper) with a fatty acid is recommended by *De Nordiske Fabriker De-No-Fa Aktieselskap* as a catalytic material in the hardening of fats or fatty

\* British Patent 18,310, Aug. 9, 1912.

† *Zeitsch. f. angew. Chem.* (1914), 63, No. 7.

‡ See also *Seifen. Ztg.* (1914), 7.



acids. About 0.4 per cent of the metallic compound is used and the hydrogenation takes place at temperatures between  $100^{\circ}\text{C}$ . and  $180^{\circ}\text{C}$ .\*

Organic compounds of metals, such as metallic salts of organic acids, are employed by **Wimmer** and **Higgins** † as catalytic agents in the reduction or hydrogenation of various organic compounds; thus the copper, iron, nickel or cobalt salts of formic, acetic or lactic acid

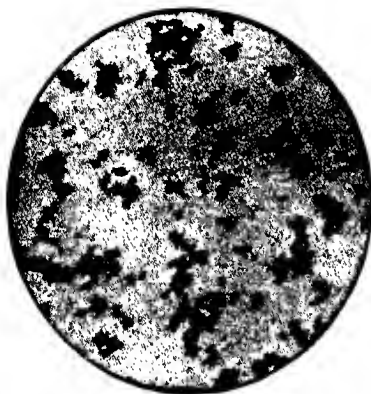


FIG. 44. — Photo-micrograph of nickel precipitated in cottonseed oil by the action of hydrogen on nickel resinolate dissolved in the oil.  $\times 100$ .

may be employed. The advantage of these compounds is that they can readily be mixed with the compound to be reduced, either in the form of a solution or as an "emulsion"; thus the compound may be emulsified with the catalyst and at the same time treated with hydrogen. It is stated that hydrogenation may be accelerated either by using the hydrogen under pressure, or by impregnating the compound to be reduced with hydrogen, and then bringing it into intimate contact with the catalyst. One detailed example is given in the specification, describing the treatment of 100 grams of cottonseed oil with hydrogen

in presence of 1 to 5 grams of nickel formate at a temperature of  $170^{\circ}$  to  $200^{\circ}\text{C}$ .

**Wimmer** makes the statement that these organic salts are not reduced to the metallic condition during hydrogenation.‡

**Bedford** and **Erdmann** § state that nickel formate yields nickel suboxide at  $210^{\circ}\text{C}$ ., while metallic nickel is formed at  $250^{\circ}\text{C}$ ., and that nickel acetate, oleate and linoleate behave in a similar manner.

**Higgins** || uses nickel or zinc formate in the reduction of organic compounds without the application of gaseous hydrogen.

Several other methods of producing catalyzers have been the sub-

\* J. S. C. I., 1914, 324.

† French Patent 441,097, March 8, 1912.

‡ Seifen. Ztg. (1913), 1301.

§ Zeitsch. f. ang. Chem. ref. (1913), 751.

|| Chem. Ztg. Rep. (1913), 680; British Patent 23,377, Oct. 12, 1912.

ject of the patents as, for example, that to **Crosfield** \* in accordance with which kieselguhr and the like is impregnated with a solution of nickel sulfate and the impregnated material treated with alkali hydrate to precipitate nickel hydrate in and on the porous material. The product is then well washed, dried and reduced. If kieselguhr is used the powder should contain about 30 per cent of metallic nickel.†

A similar procedure is the subject of a patent to **Kayser**.‡ In this case, however, the nickel sulfate or other nickel salt in concentrated solution may be used in an amount to saturate kieselguhr while leaving it in an apparently dry condition, when it is incorporated with a molecular proportion of powdered carbonate of soda and the mixture thrown into boiling water, dried and reduced.

Kayser states that there are various known ways for producing metallic powders in a state of fine division. Nickel powder, which for many purposes is recognized as the most potent catalyzer technically available, is, for example, most conveniently produced by acting upon such nickel compounds as the chloride, oxide, hydrate or carbonate at an adequate temperature with hydrogen. The catalytic energy of such a powder, however carefully prepared, he says, is at best an uncertain quantity; frequently it is feeble, as sometimes, for no conclusive reason, it is altogether lacking. Furthermore, powder thus produced is specifically heavy and he claims cannot be easily kept in suspension in a liquid medium like oil, when that is desired, nor can it, since it forms an almost impervious sediment, be readily separated and recovered from such liquid medium by a contrivance like the filter press. The same objections, he says, apply to nickel powder prepared by other means; and, in the endeavor to improve on these, Kayser brings a compound of nickel, such as the nitrate, oxide, hydrate or carbonate, into intimate contact with an inert, absorptive and comparatively bulky mineral substance, such as kieselguhr and infusorial earth, dries and comminutes the product, and reduces the powder thus produced. In one case he saturates kieselguhr with a solution of nickel nitrate, dries the mixture, employing in the case of the nitrate sufficient heat to expel the nitric acid, grinds the resulting product and reduces with hydrogen. Another way is to permeate or saturate kieselguhr with a solution of nickel chloride, nickel sulfate or other soluble nickel salt, enter the resulting product, with or without previous drying, into a boiling solution of carbonate or hydrate of soda or other suitable precipitant, remove the soluble salts, formed by washing, dry and comminute the residue, and reduce it as before. A third and preferred method, as stated, is to saturate the kieselguhr with a solution of nickel chloride, nickel sulfate or other nickel salt, using so much solution only as will leave the kieselguhr in an apparently dry and freely workable

\* British Patent 30,282, 1910.

† Ubbelodhe and Woronin (*Petroleum* (1911), 7, 9) prepared a catalyzer by crushing a plate of porous clay (which had been ignited) to form particles of about the size of peas. Nickel nitrate was melted and heated until water vapor ceased to be evolved. Then the clay particles were added and the mass was stirred and strongly heated to expel the oxides of nitrogen. This step was followed by reduction with hydrogen at 360° C.

‡ U. S. Patent 1,004,034, Sept. 26, 1911.

condition, incorporate a molecular proportion of powdered carbonate of soda or other powdered precipitant, throw the mixture with constant stirring into boiling water, remove the soluble salts formed by washing, dry and comminute the mixture, and reduce as before.

To develop the highest catalytic efficiency, Kayser states that the kieselguhr should become evenly and completely coated and permeated, plated as it were with a film of metal, and that a catalyzer composed of one to two parts by weight of metallic nickel and four parts by weight of kieselguhr has however proved very effective in saturating fats and oils by means of hydrogen. The author can see no advantage in permeating or impregnating the interior canals of the carrier with catalytic metal when the catalyst is to be used for hydrogenating fatty oils. The porous support used by Sabatier and Senderens, to be sure, was impregnated with reduced nickel, but these investigators directed their attention to the hydrogenation of readily volatile substances, capable of diffusing into the interior of the nickel-laden porous material.

Seeking to overcome the disadvantage of ready oxidation in the air possessed by normal catalytic nickel, Kayser \* reduces the nickel oxide or equivalent material at a temperature of 500° to 600° C. and then passes through the reduced material a brisk current of carbonic acid until the escaping gas proves no longer inflammable. By this method it is claimed that a catalyzer is secured which will remain perfectly cool on exposure to the air and even may be exposed for days without losing any of its catalytic energy, a result which probably is due to elimination of occluded hydrogen.†

Wilbuschewitch ‡ proposes to secure more rapid reduction of catalyzer by agitating it in the presence of hydrogen in a heated rotary drum. The temperature during the treatment is stated to be 500° C. Wilbuschewitch § has patented a process of regenerating spent catalysts of the nickel type, involving extraction with benzene, treating with alkali solution, acidifying, treating with sodium carbonate solution and reducing.

The recovery of catalytic material is described by Naamlooze Vennootschap, Ant. Jurgen's Vereenigde Fabrieken in British Patent 27,233, 1913.¶ The catalyzer is freed from organic matter by heating in a current of air, the material is treated with an acid to dissolve metal from its insoluble carrier and the metal is then precipitated on the same carrier.

\* U. S. Patent 1,001,279, Aug. 22, 1911.

† The Bremen-Besigheimer Olfabriken (Seifen. Ztg. (1913), 1007) recommend the exposure of catalytic material to an atmosphere of carbon dioxide, or inert gases. The catalysts produced in this manner are stated to be permanent and to possess great activity.

‡ U. S. Patent 1,016,864, Feb. 6, 1912.

§ U. S. Patent 1,022,347, April 2, 1912.

¶ Seifen. Ztg. (1914), 169.

**Bedford** and **Erdmann**\* treated a quantity of used nickel oxide catalyzer with dilute sulfuric acid. Hydrogen, accompanied by hydrocarbons of disagreeable odor, was evolved. A carbonaceous residue amounting to 6 or 7 per cent remained after treatment with the acid. Nickel oxide has been found to take up silica when used repeatedly as a catalyzer. The same absorption of silica also occurs with palladium.

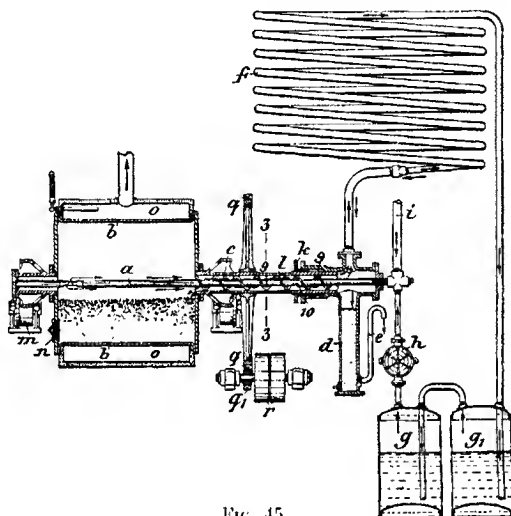


FIG. 45.

Wilbuschewitsch, in U. S. Patent 1,029,901, of June 18, 1912, describes a process of making a catalyst in which he takes, for example, nickel sulfate in the form of a solution of strength of 10 to 14 degrees Baumé, mixing this with about double its weight of an inorganic substance such as clay, asbestos, pumice stone, kieselguhr or the like, from which all soluble matter has been removed by treatment with an acid. The mixture is then treated with carbonate of soda to convert the metal salt into a carbonate. The composition is heated to about 500° C. so as to transform the carbonate into the oxide. Reduction with hydrogen is then carried out and the product is ground with oil until, as the patentee states, a strongly viscous liquid, similar in character to an emulsion, is produced.

An apparatus employed by Wilbuschewitsch,† Fig. 45, for the re-

\* Jour. f. prakt. Chem., 1913, 444.

† U. S. Patent 1,029,901, June 18, 1912.

duction of nickel compounds consists of a cylindrical drum *b* mounted to rotate on rollers *m* and provided with a heating jacket *o*. The material is charged into the drum through an inlet opening *n*. To one of the end plates of the drum a tubular shaft *c* is secured which, with its free end, is guided in a stuffing box *k* supported in a lateral stud of a tubular receptacle *d*. On the shaft a spur gear *q* is mounted which is in mesh with a pinion *g*, adapted to be rotated by means of a belt pulley *r*. By means of the gearing *q'*, *q* the drum *b* is slowly rotated, and during such rotation it is heated to about 500° C. Hydrogen is then forced into the drum through a pipe *a* located coaxially within the hollow shaft *c* and connected at one end to a tube *i*. The hydrogen is passed through the material to be reduced, and from the latter it is successively conducted through an automatically operating dust collector *9* connected to the retort, a cooling worm *f* and purifying vessels *g*, *g'* containing respectively acid and caustic soda lye, or a similar purifying medium. After thus being regenerated it is returned by means of a pump *h*. The water produced by the reduction is condensed in the coil *f* and is dropped from the coil *f* into the vessel *d* from which it is withdrawn through an overflow *e*. The dust collector *9* by means of which the hydrogen escaping from the drum is prevented from carrying along particles of dust is constructed in the form of a worm conveyor *l*. The dust moves through the hollow shaft *c* in the direction of the gas flow and owing to the difference in the speed of the gas and dust the latter is deposited on the bottom of the shaft *c*, and is conveyed back into the retort by the worm *l*.

A procedure noted in connection with Crosfields & Sons, Ltd., vs. Techno-Chemical Laboratories, Ltd.,\* disclosed as apparatus a cylindrical autoclave 1 meter high and  $\frac{3}{4}$  meter in diameter (inside measurements), with a steam jacket, and fitted with a non-conducting lining of unknown material. Nine kilograms of cotton oil were pumped into the autoclave, and 288 grams of a composition, containing a catalytic agent, were used and were mixed with the oil prior to the introduction of the mixture into the autoclave. The autoclave was then filled with hydrogen from a cylinder to a pressure of 15 atmospheres. During the operation the pressure varied from time to time according to the absorption of hydrogen. A mechanically driven circulation pump was connected with the autoclave both by its suction and delivery conduits. By means of a pump and a jet for spraying, a mixture of oil and composition containing the catalytic agent was drawn from, and forced back into, the autoclave. The iodine absorption was not determined. The composition containing

the catalytic agent was prepared from a salt of nickel. The catalyst employed was prepared as follows: About  $1\frac{1}{2}$  kilograms of nickel sulfate were dissolved in 3 liters of water, and the same weight of sodium carbonate, dissolved in the same quantity of water, and at about  $70^{\circ}$  to  $80^{\circ}$  C. was added to the nickel sulfate, which was at  $60^{\circ}$  to  $70^{\circ}$  C. The mixture was stirred for  $1\frac{1}{2}$  to 2 hours, and the precipitate was filtered off and washed with distilled water at about  $25^{\circ}$  C. for 60 to 70 hours alternately in tanks and filter press. A small sample was dried and tested to ascertain that the precipitate had been sufficiently washed. The washed precipitate was dried in hot air at  $80^{\circ}$  to  $85^{\circ}$  C., and was calculated to weigh 720 grams. It was then roasted in a pan for about 15 minutes over an open Bunsen gas burner, and the weight after roasting was calculated to be about 380 grams. The product was heated to about  $300^{\circ}$  C. for about 6 minutes in a current of hydrogen in revolving glass tubes slightly inclined, the precipitate being introduced at the higher end and through a spiral glass tube, and the hydrogen at the lower end. The product, which weighed 288 grams, was directly introduced into a small quantity of oil, which was mixed with the 9 kilos the following day.

Catalyzers said to possess high activity are produced by mixing with oil a base-metal compound of an easily-reducible character and yielding the catalytic metal on reduction, heating and bringing a reducing gas under pressure into contact with this mixture.\*

Nickel carbonyl is employed by Franck † to form catalytic material by precipitation of nickel from the carbonyl in an oil menstruum in the presence of solid material. The latter may be kieselguhr or nickel or copper oxides or reducible metallic salts. The solid material is heated with the oil and nickel carbonyl conducted into the mixture.

Eldred ‡ does not regard a finely-divided catalyst as desirable as one having a catalytic metal welded to a heat-conducting support. He states that since the amount of such catalytic action performed in a given time unit in a body of gas is strictly proportionate to the exposed surface of catalyzing metal, it is customary to use such metals in finely-divided form, sometimes as masses of powder and sometimes as powders adhering to and held by inert porous materials, such as asbestos, glass wool and the like, but that these expedients while giving great surface to a given amount of metal do not give a proportionately great exposure of such metal to the gases or vapors to be treated. It is substantially impossible to drive or distribute gases

\* Seifen. Ztg., 1913, 1298.

† Seifen. Ztg., 1913, 1271.

‡ U. S. Patent 1,043,580, Nov. 5, 1912.

uniformly throughout a body of powder, and in passing gases over a body of such powder it is substantially only the top layers of the powder which display a maximum activity, underlaying layers not functioning to any great extent. Use of very thin layers of powder of course necessitates unduly extended shelf surface. Eldred observes that nearly all catalyses are exothermic reactions, heat being developed by the action, and frequently the amount of heat is rather large. And as it is usually desirable to work within comparatively narrow temperature limits, keeping and maintaining the catalytic metal within a few degrees of some definite temperature, this evolution of heat may become a serious matter. Nearly all the catalytically acting metals in the form of powders are relatively poor conductors of heat. When, for example, platinum is distributed through a mass of such a heat insulator as asbestos, it is very hard to prevent the accumulation of reaction heat in the metal. Hence Eldred proposes a catalytic body comprising the catalytic metal in the form of a very thin continuous layer or film supported by masses of better heat-conducting metals weld-united to such layer or film and therefore in absolute metallic union therewith so that by controlling the temperature of the carrying metal the temperature of the film or layer can also be controlled. A catalyst may be made by welding a sheath or coating of platinum on a billet of copper or steel and "coextending" the joined metals to form wire or sheet metal. If 3 to 10 per cent of platinum be placed on the original billet and coextension be performed with care, the wire, sheet or leaf metal formed will also have 3 to 10 per cent of platinum, but this thickness in such coextended ware will correspond to an extremely tenuous layer. Cobalt and nickel may be united to steel or copper billets, and the duplex or compound billets extended in similar manner to produce catalysts having film coatings of cobalt or nickel. The cobalt or nickel may be united to the underlying core metal directly or through a linking layer of another metal such as gold, silver or copper. Eldred mentions the cobalt and nickel catalyzers as useful in hydrogenation reactions.

In the preparation of a catalytic body Ellis \* recommends the use of wood charcoal which possesses the property of absorbing or occluding hydrogen and when incorporated with nickel or other metal catalyst serves as an activator and storehouse of hydrogen. If nickel is used, a ratio of one part of metal to four parts of charcoal is best not exceeded. The metallic compound may be precipitated more or less on the surface of the charcoal particles by wetting the latter with a solution of a precipitant and adding a solution of a nickel salt. Pre-

\* U. S. Patent 1,060,673, of May 6, 1913.

cipitation under these conditions is largely external. Exposure of the composition to the air after reduction is to be avoided.\*

Müller † finds the catalytic activity of iron and nickel, especially in connection with processes for the introduction of hydrogen into glycerides of unsaturated fatty acids, is considerably augmented and caused to resemble in activity the catalytic properties of the noble metals, such as palladium, if the former metals after ignition in hydrogen are heated in a stream of carbonic acid gas in order, apparently, to destroy the metal hydrides which are formed and convert the catalyzer into the pure metal. Müller says the process also makes possible the elimination of finely-divided catalyzer, whose production and application the patentee states is accompanied with many difficulties, and its replacement by coarse fragments of metal, such as filings and shavings of iron, nickel and copper, first igniting the latter in hydrogen and then in carbonic acid gas. He states that common iron filings caused a reduction of the iodine number of only 2½ per cent in two hours, while using filings which had been treated with carbon dioxide the iodine number was reduced 25 per cent.

When nickel hypophosphite solution is boiled, metallic nickel is precipitated, under some conditions as thin metallic leaves; under other conditions as a fine powder. The latter form acts catalytically on sodium hypophosphite in solution giving acid sodium phosphite with evolution of hydrogen. The powder form is obtained by dissolving 20 grams nickel sulfate in 100 cc. water, heating on a water bath, introducing in one addition 70 grams sodium hypophosphite and stirring. At the end of one hour reduction is complete. Distilled water is added, the nickel material is allowed to settle and is washed by decantation.‡ Palladium prepared in a somewhat similar manner decomposes sodium hypophosphite very effectively.§

On account of the relatively low degree of sensitiveness of nickel oxide catalyzers to the usual catalyzer poisons Erdmann || was able to readily hydrogenate Japanese fish oil containing a high content of free fatty acid and also certain sulfur-containing oils, such as Egyptian cottonseed oil.

If the hardening operation is interrupted before the reaction is com-

\* See also Ellis, U. S. Patent 1,088,673, Feb. 24, 1914.

† Seifen. Ztg. (1913), 747; French Patent 540,703 (1912); British Patent 22,092, Sept. 28, 1912, to Müller Speisefettfabrik.

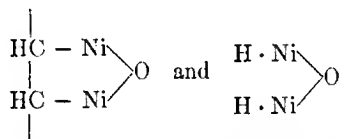
‡ The author has noted that this precipitated nickel material is catalytic and readily acts to harden cottonseed oil at a temperature of 210° C., or thereabouts, with hydrogen at atmospheric pressure.

§ Breteau, Bull. Soc. Chim. (1911), 9, 515-519.

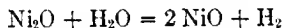
|| Chem. Ztg., 1913, 1142, 1173 and 1195.



plete, and the catalyzer collected by centrifuging, extraction with benzol or other solvents shows the rate of removal of the residual fatty substances from the catalyzer to be very slow. The fat clings strongly to the catalytic body. On the contrary when the reaction is at an end the catalyzer separates in a flocculent condition. Because of this, Erdmann is of the opinion that the oxide and unsaturated fat form a loose addition compound which is subsequently split by hydrogen. Analysis of the black nickel material obtained by extracting the fat from used catalyzer shows several per cent of carbon to be present, apparently united to the nickel as a kind of carbide. The greater portion of the used catalyzer consists of a mixture of nickel oxide and suboxide. The latter is looked upon as  $\text{Ni}_2\text{O}$ , described by Bellucci and Corelli.\* The hydrogen transference probably takes place in one of two ways: either an intermediate phase represented by the compounds



is formed (the latter compound carrying its hydrogen very loosely bound); or a decomposition of water may take place in accordance with the reaction



yielding hydrogen in a nascent state which is assumed to unite with the unsaturated fat, while the nickel oxide formed is reduced to the suboxide by hydrogen in the molecular condition. Which of these views is correct can be ascertained only by further investigations. Hydrated nickel oxide or nickel carbonate may be used in place of the oxide, and under some conditions apparently also nickel salts such as the formate and acetate. These salts act as hydrogen carriers only after the acid radical has been split up and the free metallic oxide formed.

The conclusion is reached by Bedford and Erdmann † that some of the organic salts of nickel act like nickel oxide as catalyzers and form in fact nickel oxide by decomposition when heated in the presence of hydrogen. A number of tests were carried out using nickel formate, acetate, oleate and linoleate. In one case 200 grams of cottonseed oil were heated to 253° C. with nickel formate (equivalent to 2.4 grams

\* Atti. R. Accad. dei Lincei, 22, I, 603 and 703.

† Jour. f. prakt. Chemie, 1913, 449.

NiO), and hydrogen passed into the mixture. The oil quickly darkened due to the formation of finely-divided nickel and nickel oxide. After one and one-half hours the solidifying point of the fatty product was  $51.2^{\circ}\text{C}$ . 200 grams of cottonseed oil, 6 grams of nickel acetate and 20 cc. of water were heated and hydrogen passed therethrough. The temperature was brought to 215 to 220 degrees. The acetate retained its green color unchanged and no hardening of the oil was observed. The temperature was then raised to 240 to 250 degrees when the mixture turned black and in one and one-half hours the solidifying point of the hardened oil was 49 degrees. 250 cc. linseed oil with 6.3 grams of nickel linoleate (equivalent to 1.2 gram NiO) was treated with hydrogen at 2.65 degrees for three hours yielding a product having a solidifying point of  $44.5^{\circ}\text{C}$ . The catalyst at the close of the test consisted of nickel oxide and suboxide and nickel soap. Using 11.5 grams of nickel oleate to 200 grams of cottonseed oil it was found that the black coloration occurred above 220 degrees. Hydrogenation was carried on at 250 degrees and after two hours the solidifying point was 41 degrees. On the glass walls of the reaction flask a brilliant mirror of metallic nickel formed, which in the course of time separated in coarse flakes.

A catalyst which remains easily in suspension is prepared according to the **Bremen-Besigheimer Ölfabriken** \* by incorporating a metal salt with an inorganic carrier and drying this product in the presence of the unsaturated material which is subsequently to be hydrogenated, or for that matter with any suitable indifferent liquid. The mixture is treated so as to expel all of the water and a part of the volatile acid of the salt which otherwise might become free and act injuriously during the reduction process.

By this removal of water and acid the catalyst is put into such a condition that it is capable of remaining suspended in oils and fats. In the application of the catalyst for the reduction of the latter a carrier, such as kieselguhr, asbestos and the like, is treated with a solution of a metallic salt, such, for example, as nickel acetate. After drying the material it is ground with a quantity of oil so as to yield the catalyst in an extremely finely-divided condition and disseminated through the oil vehicle. The water and acetic acid are now removed by heating the mixture to  $150^{\circ}$  to  $200^{\circ}\text{C}$ . in a closed vessel fitted with an agitator and vacuum pump. After the volatile material has been removed by such a treatment, hydrogen is conducted through the resulting product.†

\* Zeitsch. f. angew. Chem. (1913), Ref. 604.

† A form of treatment of oil and catalyst with hydrogen, as disclosed by the Besigheimer Ölfabriken, is noted in Seifen. Ztg. (1913), 1007.

**Higgins** \* states that the conversion of unsaturated fatty acids or their glycerides or other unsaturated compounds into the corresponding saturated compounds, by means of hydrogen in presence of finely-divided nickel or other metal, is accelerated by the presence of formic acid or other volatile organic acid. From 1 to 2 per cent of formic acid, calculated on the weight of unsaturated material, has been found a suitable proportion. The hydrogen may be passed through a vessel containing the volatile acid before admitting it to the mixture of unsaturated compound and metal.

According to **Wimmer** and **Higgins** † catalytic material may be prepared from nickel salts, such as nickel formate, by mixing with a protecting material, the latter, for example, being an oily body, and then reducing the salt to yield the nickel in a metallic condition. The oil serves to preserve the catalytic properties of the reduced substance.

**Wimmer** has observed that the content of free fatty acid is increased by hydrogenation and has offered as a remedy the addition of drying agents to the catalytic material. Ignited sodium or magnesium sulfate are recommended for the purpose. In hardening cottonseed oil **Wimmer** uses 3 to 10 per cent of sodium sulfate and 2 to 3 per cent of nickel formate calculated on the weight of the oil. He found a sample of peanut oil containing 0.5 per cent of fatty acid, after hardening in this manner, to contain 0.42 per cent of fatty acid, while without an addition of sodium sulfate the acid content was 0.72 per cent.‡

A flaky form of nickel catalyst is brought forward by **Hagemann** and **Baskerville** § to replace nickel supported on an inert carrier. They observe that the application of the latter type of catalysts involves a number of technical difficulties; for instance, on account of their finely-divided state, such catalysts cannot be readily and satisfactorily separated and recovered from the fats, and, owing to their density, do not remain well suspended in the oil treated, when such suspension is desired. The use of a metal precipitated upon an inert carrier, such as kieselguhr, they note, has not given entirely

\* British Patent 18,282, Aug. 8, 1912.

† French Patent 454,501, Feb. 18, 1913. When nickel formate is used, it serves both as reducing agent and as catalyst; with zinc formate, addition of a known catalyst, such as palladium chloride, is desirable. The temperature used is preferably about 20° C. below that at which the formate would decompose into the oxalate at the pressure existing during the operation. (**Higgins**, British Patent 23,377, Oct. 12, 1912.) **Wimmer** and **Higgins** (*Seifen. Ztg.*, 1914, 7) state that the metal salts of organic acids may be used for the hydrogenation of various organic compounds of an unsaturated nature in addition to oils and fats.

‡ *Seifen. Ztg.*, 1914, 390.

§ U. S. Patent, 1,083,930, Jan. 13, 1914.

satisfactory results, probably for the reason that only a small part (one side) of the film of the precipitated metal comes into actual contact with the liquid to be reduced and the hydrogen, and the remainder of the metal is consequently inactive, since the reacting materials cannot come into contact therewith. Other stated objections to the use of such a catalyst are that the process of revivification is quite an expensive undertaking, since the metal must be dissolved in an acid, and reprecipitated upon kieselguhr; that it is difficult to obtain a catalyzer by precipitation and reduction methods, which is free from oxides and other impurities; and that fatty oils hydrogenated with such finely-divided catalyzers will contain metallic soaps, such as soaps having a nickel base, which are undesirable from economic and hygienic standpoints. Hagemann and Baskerville observe that metals having catalytic activity, such as nickel, or cobalt, brought into a state of extremely thin films, or flakes, by mechanical, chemical or galvanoplastic processes, as, for example, by the method shown by Edison,\* offer technical advantages as catalysts in the hydrogenation of fatty oils. These films, or flakes, are obtainable in a state of high purity, and may be employed either in the metallic (pure) state or after being partially oxidized. Films can readily be prepared, having a thickness of from one twenty-thousandth to one forty-thousandth of an inch, and accordingly the efficiency of a given weight of a catalytic metal, for example, nickel, when applied in this form, is high, owing to the large amount of exposed surface. Such films, or flakes, will, on account of their extreme thinness, readily float and remain evenly distributed throughout the whole mass of fats or oils.† The separation of the hardened products from the flaky nickel, cobalt, etc., is said to be accomplished without difficulty. In the revivification and recovery of the catalyzer for subsequent use it has been found that flaky metals, as nickel, etc., admit of economical treatment, for the flakes retain their physical form. In this revivification the flakes, or films, from which the fat has been removed (for example, by extraction with a suitable solvent) are subjected to superficial oxidation followed by reduction with hydrogen at, say, 300° C., or higher, in a current of oxygen or air, or by treatment with oxidizing agents in liquids in which the metallic flakes are suspended. In such a manner Hagemann and Baskerville state they can repeatedly produce freshly-reduced surfaces to both sides of the metal flakes, or films, without

\* U. S. Patent 865,688. See also 821,626.

† The author has made use of a form of flaky nickel derived from nickel carbonyl in hydrogenating oils and has found this form of the metal to be satisfactory from the catalytic standpoint.

having recourse to conversion of the metal into a soluble salt, precipitating, igniting and reducing.

Another method\* of forming a catalyzer involves the utilization of the disintegrating effect of an electrical current or arc between a pole or poles of nickel immersed in a vehicle offering considerable resistance to the electric current, such as water, or aqueous solutions, thereby producing nickel material in a finely-divided condition, requiring little or no further treatment to serve as a catalyzer. For example, two electrodes of pure nickel in bar or rod form are connected one to the positive and the other to the negative pole of a source of electricity. The ends of the nickel rods are dipped in water and brought in contact, then separated so as to form an arc under the water. This results in the production of nickel material usually of a brown to blackish color in a state of more or less fine division, some of this material often being so fine and flocculent as to remain suspended in water for several days. Distilled water should preferably be used though under some circumstances saline solutions may be employed. By the use of distilled water the introduction of contaminating bodies is practically or entirely avoided.

Careful regulation of the arc is desirable in order to avoid melting away particles of nickel in the shape of large fragments which are not useful for the present purpose, although some coarse material is usually formed. When the product contains such heavy nickel particles it may be levigated and the lighter sludge separated from the heavy nickel residue. The sludge is evaporated to dryness when a very light nickel material is obtained, which may be used at once as a catalytic body or may first be reduced in hydrogen. Or, the wet sludge may be heated with oil to expel the water in order to produce a form of nickel which remains suspended in oil for a long period and this may be used as catalytic basis. In such a case it is usually well to heat to 230 to 250° C. in the early stage of the hydrogenation treatment and after a time the temperature may be reduced to 200 degrees and lower.

**Boberg** † prepares a catalyst by reduction with hydrogen of a metallic compound, such as ignited nickel carbonate, under such conditions that the resulting product is a complex compound of one or more suboxides of the metal. The preferred range of temperature during reduction is from 230° to 270° C., the material being heated for a longer period the lower the temperature employed. It is stated that unnecessarily protracted heating should be avoided as leading to a more complete reduction with loss of activity in the product.

The product may be collected for immediate use in the medium in

\* Ellis, U. S. Patent 1,092,206, April 7, 1914.

† U. S. Patent 1,093,377, April 14, 1914.

which it is to be used, e.g., oil, but if not required at once slow oxidation in the atmosphere can be allowed, provided local overheating is prevented (which leads to excessive oxidation) and the material can then be kept without special precautions against oxidation and restored to full activity when required. For instance the material may be collected in water and then filtered therefrom and allowed to dry in the air or may be collected in an atmosphere of hydrogen, which is then slowly replaced by oxygen or air.

In order to prepare it for use the material only requires to be heated for say one to two hours at about  $180^{\circ}\text{C}$ . in an atmosphere of hydrogen or the catalyst may be treated with hydrogen when in suspension in a suitable liquid. When the catalyst is used for hardening fats or oils no special treatment of this kind is necessary as the catalyst acquires its full activity in the early stages of the process.

The catalyst may be prepared by reducing to nickel as completely as possible one of the oxides of nickel and oxidizing this product with air or oxygen diluted with an inert gas, the proportion of oxygen being regulated to avoid local overheating. This oxidizing action can be carried out at between  $300^{\circ}$  and  $600^{\circ}\text{C}$ .

Boberg states that he has "made experiments with various products of reduction and has obtained the following results: The product of reduction of such a composition that an ultimate analysis gives a proportion of nickel to oxygen corresponding to an imaginary formula  $\text{Ni}_{0.5}\text{O}$ , i.e., but little suboxide, produced, in a certain time, hardening of a liquid fat up to a melting point of  $40^{\circ}\text{C}$ ., whereas, a product corresponding to an imaginary formula  $\text{Ni}_{2.65}\text{O}$  gave in the same time and for the same material hardening corresponding to a melting point of  $58^{\circ}\text{C}$ . It appeared, however, that with a lesser proportion of nickel in the product, i.e., a composition that apparently indicated the presence of higher oxides, the product was less active, while, at the same time, compounds containing even higher proportions of metallic nickel than that first specified above, viz.,  $\text{Ni}_{0.5}\text{O}$ , were still less active than the latter."

Boron may be used as a catalyzer according to Hildesheimer.\* If the material is a gas it is simply mixed with hydrogen and passed over the boron material; if liquid, it is mixed with boron and hydrogen is passed through it. When the addition of hydrogen is completed the boron is separated by filtration and is ready for use again. The catalytic action is assumed to depend upon the intermediate formation of boron hydride  $\text{BH}_3$ . The rate of conversion is influenced by the temperature and pressure as well as the amount of boron. Cottonseed oil and other unsaturated compounds, such, for example, as ethyl-

\* Zeitsch. f. angew. Chem. (1913), Ref. 583.

ene, add hydrogen under these conditions. In place of boron some of its compounds, such as boron hydride, and metallic compounds of boron, such as aluminium boride, may be used. Gases containing hydrogen may be used in place of pure hydrogen.\*

On the large scale the manufacture of catalyzers by reduction of the oxide of a metal in a current of hydrogen has been found to bring with it a train of difficulties. A method of reducing catalyzer in a continuous manner† which simplifies the operation to a considerable extent is shown in Fig. 46. A charge of the material to be reduced

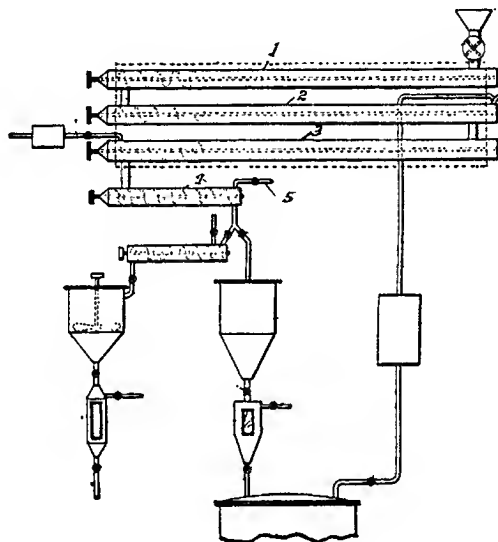


Fig. 46.

is fed from the hopper and feed arrangement into a series of horizontal parallel conveyors 1, 2, 3 and 4 into which a current of hydrogen gas is introduced by the pipe 5. These conveyors connect one with another alternately so that the material travels in one direction through a given conveyor, then falls into the conveyor beneath and travels in

\* A process of hydrogenation involving the use of chloride of mercury is described in an Austrian patent application noted in *Seifen. Ztg.* (1913), 1413. According to the method set forth fatty acids or their glycerides are heated to a temperature below 180° C. with a mixture of a difficultly reducible inorganic salt of a base metal in company with chloride of mercury and at the same time hydrogen or other reducing-gas mixture is passed through the oil.

† Ellis, U. S. Patent 1,078,541, Nov. 11, 1913.

an opposite direction. At the same time the material is heated to the proper temperature of reduction and throughout its travel is in contact with a counter-current of hydrogen. Thus, the more nearly reduced material is constantly progressing into a zone of purer hydrogen, while the fresh raw material meets hydrogen charged with steam. In this manner conditions of reduction are so facilitated that the use

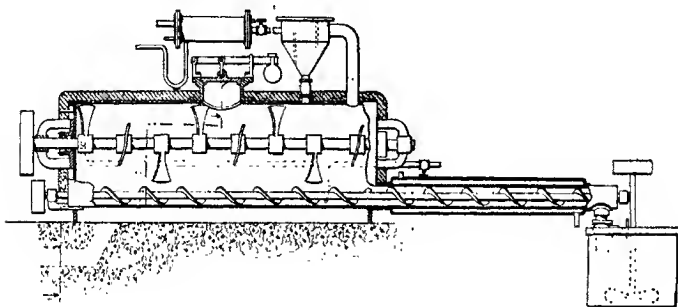


FIG. 47.

of a great excess of hydrogen to remove the steam does not become necessary. After the catalyzer has been reduced it may be mixed with oil in another conveyor and be subsequently carried to a grinder or beating apparatus where the coarser particles are broken down.

Another form of catalyzer reducing chamber is shown in Fig. 47 and consists of a closed chamber equipped with a stirrer and with a conveyor to remove the reduced material.\*

\* Ellis, U. S. Patent 1,084,202, Jan. 13, 1914.



## CHAPTER VI

### THE BASE METALS AS CATALYZERS—Continued

Dewar and Liebmann\* observe that the temperature at which the reduction by hydrogen of oxides or hydrates of nickel, cobalt, copper and iron commences can be considerably reduced and that this is of importance as the production of catalysts at a low temperature is advantageous.

The lower temperature prevents the possibility of the new molecular aggregations of the finely-divided metals. It renders it possible to produce the catalyst and effect hydrogenation in one operation, at such a low temperature as prevents decomposition of the oils and fats. The method of Dewar and Liebmann consists in the reduction by hydrogen at a relatively low temperature of a mixture of the oxides or carbonates (either hydrated or anhydrous) of two or more catalytic metals, Ni, Co, Cu and Fe, or of a mixture of the oxides of one or more of these catalytic metals with palladium, platinum or silver in a fine state of division. A mixture of the oxides of one or more of these catalytic metals along with silver oxide can also be employed. A mixture of anhydrous oxides may be obtained from the hydrates or nitrates or carbonates by heating. In practice they find that in preparing the anhydrous oxides from a mixture of nitrates, the use of a mixed aqueous solution gives on evaporation a product which, after heating, is particularly suitable for the reduction.

The following examples are given by Dewar and Liebmann:

(1) A solution prepared by dissolving 98.2 parts of nickel nitrate ( $6\text{H}_2\text{O}$ ) and 9.3 parts of copper nitrate ( $6\text{H}_2\text{O}$ ) is heated and precipitated while hot with a slight excess of caustic soda. The mixture is then boiled and the precipitate collected on a filter and washed with hot water until free from soluble salts. It is subsequently dried on the water-bath and the drying is finally completed in an oven at a temperature of about  $130^\circ\text{C}$ . The reduction by hydrogen is nearly completed after about two hours at about  $170^\circ\text{C}$ .

(2) A solution prepared by dissolving 44.6 parts of cobalt nitrate (crystals) and 4.65 parts of copper nitrate (crystals) is heated and precipitated with a slight excess of caustic soda. The mixture is then boiled and the precipitate collected on a filter and washed with hot water until free from soluble compounds, then dried on the water-bath. The reduction by hydrogen is practically complete after four hours at about  $180^\circ\text{C}$ . The reduction product contains 10 per cent copper and 90 per cent of cobalt.

(3) A solution prepared by dissolving 65 parts of iron nitrate (crystals) and 4.65 parts of copper nitrate (crystals) is heated and precipitated while hot with a slight excess of caustic soda. The mixture is boiled, filtered and washed

\* J. S. C. I., 1914, 797, British Patent No. 12,981, 1913; U. S. Patent No. 1,295,692, June 4, 1918. See also U. S. Patent No. 1,156,068, Oct. 12, 1915 to Ellis.

until free from soluble compounds, then subsequently dried on the water-bath. The reduction by hydrogen is practically complete after two and one-half hours at from about 275° to 320° C. The reduction product contains 10 per cent of copper and 90 per cent of iron.

(4) A solution of .218 part of platinum chloride and 49.1 parts of nickel nitrate (crystals) is poured into a boiling aqueous solution containing thirty parts of caustic soda and two parts by weight of 40 per cent formalin. The boiling is continued for some time and the precipitate separated is collected on a filter, washed until free from soluble salts and dried on the water-bath. On being treated with hydrogen, the reduction is practically complete after four hours at about 200° C. and the reduction product contains 1 per cent of platinum and 99 per cent nickel. Mixtures of nickel hydrate and palladium can be prepared in like manner.

(5) A solution of 89.2 parts of nickel nitrate (crystals) and 3.16 parts of silver nitrate is poured into a warm solution of 30 parts of caustic soda and boiled. The precipitate is then collected on a filter, washed until free from soluble compounds and dried on the water-bath. The reduction of this compound by hydrogen is practically complete in about two hours at about 200° to 210° C. and the reduction product contains 10 per cent of silver and 90 per cent of nickel.

(6) Forty-two parts of kieselguhr are impregnated with 100 parts of a solution containing 12½ parts of nickel nitrate (crystals) and 12½ parts of copper nitrate (crystals). A solution of 11 parts of sodium carbonate in 100 parts of water is added and the whole well stirred together. The precipitate is collected on a filter, washed thoroughly until free from soluble salts and dried on the water-bath. The reduction is practically complete after one hour's treatment with hydrogen at about 170° C., and the reduction product contains after treatment for another hour at about 180° C. 99 per cent of metallic contents.

A metal powder catalyzer is prepared by Ellis\* by reducing nickel hydrate suspended in heated oil through which hydrogen is passed. Composite catalyzers such as nickel and cobalt or copper are prepared in a similar manner. The nickel-copper catalyzer is useful in hydrogenating fish oil. It also has been found more active than nickel alone in hydrogenating oleic acid.

Kayser† refers to the use in catalytic processes, of nickel compounds, such as the carbonate, hydrate, oxide, formate or acetate and notes that before these bodies become capable of transmitting hydrogen, they have to suffer preliminary changes, of a hitherto undefined nature. Such changes, he claims, do not take place at a temperature materially below 250 or even 275° C. Once formed, the catalyzers will transmit hydrogen to fatty bodies at a more moderate temperature.

Excessive heating of all but a limited quantity of fatty material may be avoided, in the practice of fat-hardening, by preparing a concentrated fatty

\* U. S. Patent No. 1,150,068, October 12, 1915.

† U. S. Patent No. 1,236,446, August 14, 1917.

catalyzer-paste or catalyzer-cake, which is thereafter used at a lower temperature for the conversion of unsaturated fatty bodies in presence of hydrogen; or the preliminary treatment of the catalyzer stock may be carried out at relatively high temperatures in another medium, such as paraffine wax, the resulting catalyzer being thereafter isolated. These methods, however, are stated to be not without inconvenience and drawbacks. Kayser observes that these nickel compounds, and some others not hitherto available, can readily be converted into catalyzers of superior activity and longevity, and this at a temperature not exceeding  $180^{\circ}\text{C}.$ , when the preliminary treatment is carried out in presence of a small quantity of certain finely-divided metals, and that fatty bodies can, at a moderate temperature, be conveniently saturated with hydrogen to any desired degree if they are submitted to the action of hydrogen in the simultaneous presence of the usual amount of nickel compound and of a comparatively small amount of finely-divided auxiliary catalytic metal, such as would by itself exercise upon the fat but very slight action, or no action whatever.

Thus, if cottonseed oil be agitated with hydrogen at  $180^{\circ}\text{C}.$  in presence of about 2.5 per cent of commercial nickel carbonate, the mixture does not change color, and no hardening of the oil takes place. If the oil be similarly treated with gas in the sole presence of about  $\frac{1}{2}$  g. of so-called "atomic" copper, prepared by the action of zinc dust on copper sulphate solution, a like negative result is registered. If, however, quantities of nickel carbonate and copper metal be simultaneously present, the charge rapidly darkens and becomes progressively hardened, showing after two hours a melting-point of  $46^{\circ}\text{C}.$ , after three hours,  $52^{\circ}\text{C}.$ , and after four hours,  $56^{\circ}\text{C}.$  When finally freed from suspended catalyzer by filtration or other mechanical means, the fat will set to a white, tasteless and odorless, brittle solid. The recovered catalyzer can repeatedly be used in the same manner; its activity will at first be found to increase and then to slowly decline. Similar, but somewhat inferior, results are stated to be produced with nickel hydrate in place of carbonate, while the oxides and organic nickel salts do not readily cooperate, or entirely fail, with copper. Such organic compounds, as the formate, on the contrary are, like the hydrate, the carbonate and the oxide of nickel, rapidly transformed and activated by a small quantity of catalytic metallic nickel, produced by dry reduction of the oxide, hydrate or carbonate in a current of hydrogen. Even the oxalate, otherwise quite stable, at  $275^{\circ}\text{C}.$  is said to be readily transformed into an efficient catalyzer. For example, 250 g. of cottonseed oil, agitated with hydrogen at  $180^{\circ}\text{C}.$  in presence of 3.5 g. of active nickel-powder, are in three hours hardened to a melting-point of  $37^{\circ}\text{C}.$ ; in the simultaneous presence of 7 g. of nickel hydrate the charge rapidly turns grey and, when filtered after three hours running yields a white fat, melting at  $54^{\circ}\text{C}.$  In the same manner, cooperation of 0.5 g. nickel-powder with 12.5 g. nickel oxalate yields in three hours a white fat, melting at  $54^{\circ}\text{C}.$  The reactions described may frequently be facilitated by using, instead of the pure nickel compound and the pure auxiliary metal, the like bodies, deposited upon kieselguhr or a similar indifferent support. The chemical nature and the appearance of the catalyzer produced by the process, varies with the auxiliary metal employed. Nickel is stated to yield a grey, non-metallic catalyzer, while copper produces a black body, developing with hydrochloric acid far less hydrogen, than what would correspond with the hypothetical sub-oxide  $\text{Ni}_2\text{O}$ .

A catalyzer used by Lubeck and Payet\* is prepared by mixing cuprous chloride

\* J. S. C. I., 1909, 830. French Patent No. 397,746, March 5, 1908.

with native hydrated cobalt oxide and heating in vacuo to 450° C. A current of hydrogen or of illuminating gas, previously heated to 120° C., is then passed over the material. By treatment with hydrochloric acid cuprous chloride is dissolved and a double chloride of cobalt and copper precipitated, or a mixture of hydrated cobalt chloride and copper chlorides, according to the conditions of heating in hydrogen. The precipitate is allowed to settle on pieces of pumice which are afterwards dried.

Silicious material, known as monox or silicon monoxide, which is of a very light and voluminous character and is prepared in an electric furnace was tested in the author's laboratory as a supporting material for nickel in the preparation of a catalyzer.

By means of a solution of nickel nitrate the monox was saturated with the nickel solution and the mixture ignited until red fumes ceased to be evolved. The product was then reduced to a fine powder and heated for one hour in a current of hydrogen at a temperature of 340° C. The reduced catalyzer was preserved under oil. The proportions used in preparing the materials were 10 parts by weight of nickel nitrate  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  to 8 parts of monox. Cottonseed oil containing 5 per cent of this catalyzer or approximately 1 per cent of the reduced nickel was heated for 3½ hours to 174°–180° C., while a continuous stream of hydrogen was passed through the oil and the melting-point of the hardened product which resulted was 48.2° C.

Fresenius describes a process of hydrogenating organic compounds such as unsaturated oils which consists in mixing the oil with pure powdered carbon (Kohlenpulver) heating and conducting in the presence of hydrogen over contact material such as porous carbon, metal carbides or other known contact materials. The hydrogenation is in this manner carried to completion in a short time. Furthermore, this process is stated to avoid high temperatures common to other processes so that the fat is not injured and hence the product is well adapted for edible purposes.\*†

A method of preparation of a nickel-charcoal catalyzer is described by Ellis.‡

The charcoal may be purified by washing with dilute nitric acid and also in some cases with alkali so as to remove undesirable mineral matter; finally washing with distilled water, thereby obtaining a good, clean material. Nickel hydroxide, preferably freshly prepared in a state of purity is dissolved in a concentrated ammoniacal solution and the charcoal is treated with the solution. Only approximately enough ammonia is used to dissolve the nickel hydrate and the quantity of the latter with reference to the amount of the charcoal is prefer-

\* Seifen. Ztg., 1914, 1282.

† The use as catalyzers of such substances as iron oxide, pumice stone, bone black, charcoal or copper oxide is recommended by Ellis and McElroy (U. S. Patent No. 914,251 of March 2, 1909), in connection with the manufacture of chlorinated naphthalene.

‡ U. S. Patent No. 1,156,674, October 12, 1915.

ably proportioned to give a product having from 10 to 30 per cent of nickel. After the nickel solution and the charcoal have been incorporated the material is dried when the ammonia evaporates and the product is then reduced with hydrogen.\* †

A catalyzer, for hydrogenating oils, described by Ittner ‡ is prepared from charcoal which has deposited throughout its structure a small amount of certain mineral bodies, as, for example, compounds of the earth metals or alkaline earth metals, such as alumina, or silicates of metals like aluminum, calcium, magnesium and cerium.

The product is stated to possess entirely different properties from ordinary charcoal, in so far as its catalytic activity is concerned, although in other respects identical with ordinary charcoal. Ittner observes that this superior catalytic activity of the charcoal treated as described is developed when it is used as the porous body upon which catalytic material, e.g., metallic nickel, active nickel oxide, or the like, is deposited, and is extraordinary in degree. In the preparation of the charcoal spruce or cedar wood may be subjected to dry distillation in a retort. Good results are obtained with both coniferous and deciduous wood. Active charcoal also may be made from other organic substances, as, for instance, cornstalks and peat. The atmosphere of the retort may be kept under reduced pressure, or the distilling operation may be expedited by means of a current of superheated steam passed through the retort, or a current of carbon dioxide gas. It is best not to use too high a temperature in making the charcoal, but it should nevertheless be sufficiently high to drive off volatile matter. After the distillation has progressed until volatile products of decomposition are no longer given off by increased heat, the resulting charcoal is allowed to cool out of contact with the air. When cool, it may then be powdered, and saturated with a dilute solution of an alkaline silicate; an 8 per cent solution of sodium silicate may be used to advantage. The charcoal thus impregnated with silicate should then be heated in a closed retort, to a dull red heat or a temperature somewhat under a dull red heat. It should then be allowed to cool to atmospheric temperature out of contact with air before being removed from the retort and may then be treated with a solution of, say, aluminum sulphate, alum, or other salt of aluminum. The support thus prepared may be washed with water, and coated or impregnated with catalytic metal, as for instance, nickel, or the active oxide. Any of the well-known methods for coating or impregnating a support with an active catalytic metal may be used. If the nickel is obtained by first saturating the active charcoal with a solution of nickel nitrate, and later igniting in the presence of the nitrate, a dilute solution of the nitrate is found to give the best results. A good way to prepare the catalyzer is to saturate the active charcoal with a solution of some nickel salt, remove the excess nickel solution by pressure or filtration, and then treat the active charcoal, coated and impregnated with nickel solution, with an excess of a dilute solution of sodium carbonate or other precipitant, whereby, Ittner states, the nickel becomes fixed within and upon the active charcoal in a form insoluble in water.

\* Finely-divided nascent carbon which forms in cracking oils acts as a hydrogenating catalyst under some conditions (British Patent No. 9,728, July 3, 1915.)

† See also U. S. Patent No. 1,174,245, March 7, 1916 to Ellis.

‡ U. S. Patent No. 1,238,774, September 4, 1917.

The excess sodium carbonate and other soluble salts should then be washed out with water, and the mass subjected to drying and to heat in a current of hydrogen gas to yield metallic nickel. Ittner also gives directions for making nickel oxide in active form, in place of the metal. A catalyzer prepared, as described, from charcoal rendered active by the treatment noted is asserted to be from ten to more than one hundred times as active in the hydrogenation of oils as a catalyzer which is in all other respects the same except for the manner in which the charcoal is prepared, and it is very much more active than catalyzers in other respects the same but which are made with the employment of kieselguhr, pumice, or other inert porous support in place of active charcoal.

A method of forming a catalyzer described by **Tamari\*** is as follows: A suitable reagent is added to a solution of such composition that not only the catalyzer is precipitated, but also a difficultly soluble carrier for the same, either simultaneously or consecutively. This procedure permits (1) the uniform distribution of the catalyzer in a finely-divided state over the carrier, (2) a ready control of the distribution of the catalyzer, (3) determination of the specific gravity of the catalytic product by the proper choice of the amount and character of the carrier, so that when it is used in a liquid medium it will float or sink or remain in suspension, as desired, and (4) the removal of moisture, when necessary, by the selection of an absorbent carrier; calcium sulphate and alumina being mentioned for the purpose.

A catalyzer adapted for use in the production of light from heavy hydrocarbons is recommended by **Valpy and Lucas.†** In its preparation a powdered metallic oxide or a mixture of oxides is heated with organic compounds of the metal.

Suitable proportions for a catalyzer for the production of light hydrocarbons from heavy hydrocarbons are: Ferric oxide, 32; nickel oxide, 7.5; carbon, 5.5; ferrous oxalate, 40; and nickel oxalate, 15 parts. The mixture is incorporated with 17½ per cent by weight of tar, briquetted, and sintered in an enclosed crucible to effect reduction, at a temperature below the melting-point of the metal. The procedure may be applied to other catalytic metals, e.g., chromium, cobalt, or manganese. The addition of small amounts of aluminum, cerium, magnesium, or other members of the alkaline earth group is an advantage in many cases, for example, a portion of the carbon may be replaced by powdered aluminum to the extent of 1.5 per cent of the total weight of the mixed powder. Other suitable mixtures are: (1) Ferric oxide, 35; manganese carbonate, 27; carbon, 3; aluminum, 5; and ferrous oxalate, 30 parts. (2) Ferric oxide, 36; nickel oxide, 15; aluminum, 3; iron tartrate, 30; and nickel acetate, 16 parts. 17.5 parts of tar are used in each case. The catalytic bodies so obtained do not appear to lose their effectiveness after continued use; in fact in some cases an increase in efficiency after a short period of use has been observed.

\* Japanese Patent No. 29,986, September 5, 1916; Chem. Abs., 1917, 529.

† British Patent No. 5847, March 7, 1914; J. S. C. I., 1915, 784.

The **Badische Co.\*** report that the hydrogenation and dehydrogenation of compounds containing carbon can be carried out rapidly and at comparatively low temperatures, by employing, as the catalytic agent, an intimate mixture of either iron, nickel, cobalt, or copper, with a high melting and difficultly reducible oxide, in particular, the oxides and oxygen salts of the earth metals, including the rare earths, and those of beryllium, magnesium, manganese, uranium, vanadium, niobium, tantalum, chromium, boron, titanium and also difficultly soluble phosphates, molybdates, tungstates and selenates of the alkaline earths, and of lithium, or the reduction products, containing oxygen, of these phosphates, molybdates, tungstates, or selenates, as for instance, the corresponding selenites. All of these compounds containing oxygen, which augment the activity of the catalytic agent, are termed "promoters."

The oxygen-containing salts of the alkaline earths and of lithium appear to have the same action as the corresponding salts of aluminum, magnesium, and the like, although lithium oxide and the oxides of calcium, barium, and strontium, are themselves not suitable for use as promoters.

An intimate mixture of the catalytic metal and a promoter is required and it is not sufficient, according to the Badische Co., merely to pack the components, for instance, nickel and alumina, side by side, into the reaction space, nor is it adequate to absorb a solution of a salt of the catalytic metal into a porous mass, such as magnesia, and then decompose the salt of the catalytic metal. Good results can be obtained by precipitating the hydroxides, oxides, or carbonates, of the components; or mixtures of salts, for instance, the nitrates of the components, can be heated to fusion. Further, it is stated that the mixture can be obtained, although not always with equal certainty and excellence, by mechanical operations, such as by grinding together as finely as possible, or by kneading in a moist state. If necessary the mixture is subsequently heated and reduced so that the catalytic metal (iron, nickel, cobalt, or copper), is obtained in a metallic condition, while the promoter always retains more or less oxygen. When the promoter is to consist of an insoluble oxide such, for instance, as aluminum oxide and titanium oxide, it is preferred to start with a soluble compound, and to precipitate, or otherwise form the insoluble oxide on the catalytic metal, or on the compound from which the catalytic metal is to be prepared. For instance, if aluminum acetate be employed to yield the promoter, aluminum oxide, the acetate can be merely heated in the presence of the catalytic metal, or a compound of the latter, so that the acetic acid is driven off, and the alumina remains. If insoluble salts, such for instance, as certain chromates, and borates, be employed as promoters, these are preferably brought into intimate mixture with the compound, which is subsequently to give rise to the metallic catalytic agent, by precipitation from suitable soluble salts. The salts which act as promoters may contain the oxide, to which the promoting action is ascribed, either in the acid constituent, or in the basic constituent, or in both the acid and basic constituents. Calcium aluminate, and aluminum phosphate, are instances of com-

\* British Patent No. 2306, 1914.

pounds of this character. In some cases, the promoter may consist of a salt, of which neither the acid constituent, not the basic constituent of itself acts as a promoter. Calcium phosphate is an example of this type.

It is particularly advantageous for the purpose of producing a very active contact mass to prepare, at least the catalytic metal, from carbonaceous salts, or mixtures of salts; for instance from carbonates, or from formates. Sometimes the action of the catalytic mixture, it is alleged, can further be increased by adding an alkaline metal compound, for instance, caustic soda, even traces of such bodies often having a favorable action. The introduction of bodies such as chlorine, sulphur, arsenic, and lead, which may, in the elementary form, act as contact poisons, is to be avoided, although these contact mixtures are claimed to be not so sensitive to the action of poisons as are the pure metals. It is consequently possible to employ as a promoter, an oxygen salt which contains one of the poisonous elements, but in which the poisonous action is counteracted by the promoting influence of the oxide; for instance, basic aluminum sulphate is observed to possess a strong promoting action. The proportion of the components employed in the catalytic mixture may be varied considerably, even an addition of 1 per cent, or less, of the promoter is stated to produce in most cases, favorable action. These catalytic mixtures can be used for the hydrogenation and dehydrogenation of compounds containing carbon and are claimed to be of particular value for the hardening of fats and fatty acids, but they can also be used for other purposes, for instance, for converting phenol into cyclohexanol and for reducing nitrobenzene to aniline, and for the conversion of oxides of carbon into hydrocarbons.

The use of mixtures containing strongly basic bodies in the hydrogenation of ats is undesirable. The presence of strong bases is, in such cases, detrimental, since they tend to saponify and very soon disappear from the contact mass.

The following are examples of how catalysts can be prepared according to the foregoing, and how they are applied in the hydrogenation of organic bodies. The parts are by weight.

1. Pour an aqueous solution of 1 part aluminum nitrate over 5 parts of nickel oxalate, evaporate the mixture and dry it and reduce it in a current of hydrogen at from 300° to 350° C. Then introduce the catalyzer, while excluding air, into a vessel, provided with a stirrer, the vessel containing fish oil. On treatment with hydrogen at, for instance, 100° C., hydrogenation takes place considerably more rapidly than if pure nickel were employed as the catalytic agent. Instead of aluminum nitrate, cerium nitrate, or cerium ammonium nitrate, can be employed.

2. Precipitate a hot solution containing nickel nitrate and aluminum nitrate with potassium carbonate, wash and dry the precipitate, heat it to 300° C., and reduce with hydrogen. Then place the catalytic mixture with soya bean oil in an autoclave, while avoiding the presence of air, heat to 80° C. and allow hydrogen to act at a pressure of twenty atmospheres while mixing the constituents. The hydrogenation takes place very rapidly. If desired the pressure can be increased, for instance, up to fifty atmospheres, or higher. In this example, good results can also be obtained if iron nitrate be employed instead of nickel nitrate.

3. Mix 13 parts of nickel hydroxide with 2 parts of magnesium hydroxide, and warm gently with concentrated formic acid free from sulphur, until the formates are obtained. Heat the mixture cautiously until dry, and then treat with hydrogen at 300° C. On treating olive oil with hydrogen in the presence



of this catalytic mixture at say, from 80° to 100° C. hydrogenation is effected more rapidly than is the case when pure nickel is used. In this example the hydroxides can, if desired, be replaced by the corresponding carbonates. Carriers such as pieces of clay can be employed, these being soaked in a melt, or solution, of nickel salts, preferably of the soluble double salts, such as nickel ammonium formate, or ammoniacal nickel carbonate, together with similar salts of the promoter, and then treated as described.

4. Make nickel wire netting into the form of loose spheres or rolls, clean these with pure dilute nitric acid, wash and moisten them with a moderately concentrated solution of aluminum nitrate; then dry and treat with hydrogen at from 300° to 350° C. The contact mass containing alumina can, for instance, be employed for the hydrogenation of linseed oil which can be allowed to trickle over the catalytic agent while the hydrogen is supplied.

5. Dissolve 85 parts of nickel nitrate and 15 parts of titanium lactate in a small quantity of hot water and precipitate by means of caustic soda, or sodium carbonate, then filter, wash, dry, and reduce with hydrogen at 300° C. and add the catalytic mixture containing titanium oxide to cottonseed oil, and treat with hydrogen at from 100° to 120° C., while keeping the mixture in motion. If desired the reaction can be carried out under increased pressure (for instance, 100 atmospheres) and in this case the hydrogenation takes place very rapidly, and completely, even at a temperature of 90° C. or lower. Further, the process can be made continuous by allowing the oil to flow over the catalytic agent in a vessel capable of withstanding pressure while simultaneously passing a current of hydrogen into, or through the apparatus. The product is drawn off while hot and allowed to solidify.

6. Take freshly precipitated nickel carbonate and add from 10 to 20 per cent of its weight of ammonium or potassium borate, which has previously been dissolved in water. Then form the mass into any desired shape, and dry and reduce it. The mixture can be employed for hydrogenating oils and fats, either at ordinary pressure or under increased pressure. If chromium oxide be used as the promoter, this can be obtained, for instance, from chromium nitrate, or from soluble chromates, by precipitation. Further, when boron oxide is employed as the promoter, the oxide, or carbonate, of the catalytic metal may be mixed with solid, or dissolved, boric acid and then be heated and reduced; or the salt of the catalytic metal, for instance, the nitrate, can be mixed with the borate of the same metal, or of a volatile or non-volatile base, and the mixture is then calcined and reduced.

7. Add two parts of dissolved potassium aluminate to a solution containing 30 parts of nickel nitrate and  $1\frac{1}{2}$  parts of calcium nitrate and introduce the whole into a boiling solution of sodium carbonate. Then filter, wash well, dry and reduce. Or, add a solution of  $1\frac{1}{2}$  parts of magnesium nitrate to 5 parts of nickel carbonate, and then add a solution of  $\frac{1}{4}$  of a part of ammonium phosphate and precipitate with caustic soda, or sodium carbonate, filter, wash, dry and reduce. The nickel catalytic agent containing calcium aluminate, or magnesium phosphate, as the case may be, can be employed for hydrogenation purposes, for instance, it may be introduced into oil which results from cracking petroleum residues and which is rich in unsaturated compounds, whereupon hydrogen is allowed to react at a temperature of 100° C. and at a pressure of eight atmospheres. The iodine number is rapidly reduced and at the same time the color and unpleasant odor diminish.

In a similar manner other contact mixtures can be employed, which contain as a promoter, for instance, calcium vanadate, barium chromate, aluminum borate, barium tungstate, or lithium phosphate, or the compounds which result on the reduction of these bodies.

8. To a hot solution of 13 parts of nickel nitrate and 2 parts of chromium nitrate, add a hot solution containing 6 parts of anhydrous sodium carbonate. Filter off the precipitate, wash it until the filtrate is free from alkali, then dry and reduce it. With the help of this catalytic agent, soya bean oil can be hydrogenized rapidly at a low temperature.

9. Suspend 40 parts of nickel carbonate in a solution containing 1 part of ammonium tungstate and then add a solution of 1 part of barium nitrate, filter off the product, wash it well, dry and reduce it at 300° C. The product can be employed, for example, for hydrogenating sesame oil at 120° C.

10. Mix to a paste 50 parts of nickel carbonate and a solution of 13 parts of calcium nitrate and then stir in a solution of 7 parts of ammonium phosphate. Filter off the product, wash well, dry and reduce at from 300° to 350° C. The product can be employed for hydrogenating fish oil.

11. Stir 80 parts of nickel carbonate into a solution of 2.6 parts of strontium nitrate, and add a solution of 2 parts of ammonium selenite. Filter off the product, wash well, dry and reduce. The product can be used for hydrogenating cottonseed oil.\*

The effect of preparation of catalytic nickel under different conditions is discussed by **Crossley** † who reproduces some curves of hydrogenation derived from experiments made by **Hehner**.

Nickel prepared from the hydroxide or from the nitrate through the oxide at 250° gave approximately the same results on whale oil, but at 180° C., the nickel prepared from the nitrate was less active. Nickel produced by strongly heating the nitrate and reducing the resulting oxide was practically without effect on linseed oil and nickel obtained from the sulphate through the hydroxide (probably containing traces of sulphur) was markedly less active than carefully purified nickel from the hydroxide. The following example, from evidence handed into court in the case of *Joseph Crosfield and Sons, Limited, v. Technico-Chemical Laboratories, Limited*, may be cited. The iodine value of an oil was decreased from 108.4 to 72.1 by treatment with hydrogen in presence of nickel obtained by igniting nickel carbonate at 400° to 450°, and reducing the resulting oxide with hydrogen at 400° C. A specimen of the same oil had its iodine value lowered to 13.2 when treated in presence of nickel prepared from the carbonate by roasting at 300° for five to six minutes, and reducing the resulting oxide with hydrogen at 300° C., for four to five minutes.

**Bosch, Mittasch and Schneider** ‡ also recommend complex compounds of fluorine as activators for catalytic iron, nickel, cobalt or copper. They give the following example: Soak 100 parts of nickel

\* *Seifen. Ztg.*, 1914, 1133; *Zeitsch. angew. Chem., Referat.*, 1915, 220; German Patent No. 282,782, December 12, 1913; *Chem. Ztg. Rep.*, 1915, 155. Austrian Patent, No. 72,758, November 25, 1916. See also U. S. Patent No. 1,271,013, July 2, 1918.

† *Pharm. Soc.* April 21, 1914; *Pharm. J.*, 1914, 92, 604, 637 and 676; *J. S. C. I.*, 1914, 1135.

‡ U. S. Patent No. 1,216,933, February 20, 1917.

carbonate in a concentrated solution of 10 parts of sodium silico-fluoride, then dry and treat with hydrogen at  $320^{\circ}\text{C}$ . Introduce the contact mass thus obtained into linseed oil, while avoiding the presence of air and treat with hydrogen at a temperature of  $120^{\circ}\text{C}$ . and a pressure of ten atmospheres. The reduction, and simultaneously the hardening, of the oil take place very rapidly.

Instead of sodium silico-fluoride, other silico-fluorides can be employed, for instance, those of aluminum, calcium, and potassium, or other fluorine compounds, as barium fluoride, calcium-boron fluoride, and potassium-titanium fluoride, can be used. Nickel wire netting can be improved catalytically by soaking it first with dilute

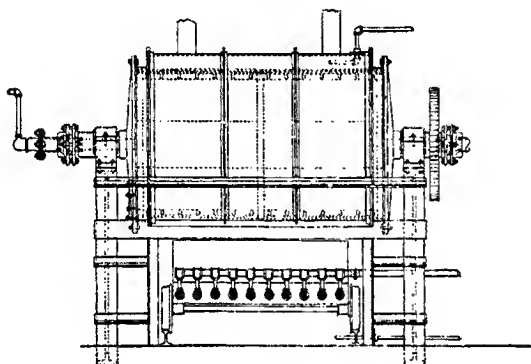


FIG. 47a.

nitric acid and then treating it with a solution of ammonium-silico-fluoride, finally adding a small quantity of aluminium nitrate and drying and reducing.

An apparatus employed by **Kayser**\* for reducing metallic oxides with hydrogen, is shown in side elevation in Fig. 47a and in vertical cross-section in Fig. 47b. It consists of a rotary drum supported by hollow trunnions, and provided with vanes for agitating the material. The latter is introduced through a manhole. A reducing gas is introduced through one trunnion and escapes through the other. Entrained matter is removed from the used gas by a trap and water seal. The drum is heated from beneath by gas burners mounted on a removable carriage. A jacket surrounds the drum forming a space through which the products of combustion pass to the stacks at the top. When the charge has been reduced, the burner carriage

\* U. S. Patent No. 1,134,745, April 6, 1915.

is removed and steam is blown around the drum until the latter has cooled somewhat. Finally water is sprayed on the drum for a brief period and the cooled contents are then removed.

**Morey** and **Craine**\* describe a form of apparatus for making catalytic material which comprises in its main features an inclined tube or conduit through which the catalytic raw material flows downwardly, either by gravity alone or by gravity assisted by a

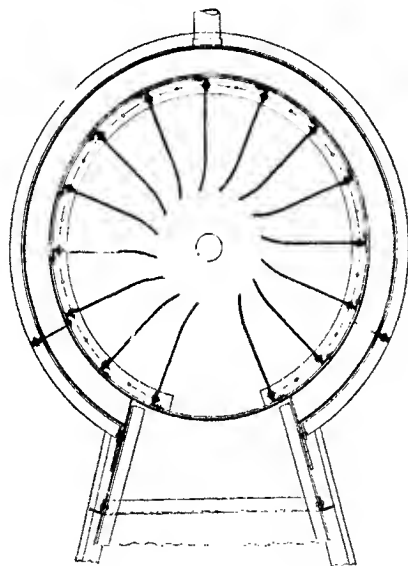


FIG. 47b.

jarring or shaking action, and through which the gas flows upwardly, the tube or conduit being heated in any suitable manner, for instance, by direct flame, superheated steam or electrical current.

In Fig. 47c is shown a side elevation of this apparatus. 10 represents the inclined tube in which the material is subjected to the action of a reducing gas, and to the upper end of which the raw material is supplied from a feed receptacle 11 by a flexible pipe 12. This inclined tube is supplied with gas from a gas holder 13 by means of a flexible pipe 14 which is connected with the lower portion of the tube. The treated material is discharged from the lower end of the latter into a closed receptacle 15 by a flexible pipe 16 without exposure to the atmosphere. The gas escapes from the upper end of the tube and is conducted by a flexible pipe 17 to a scrubbing apparatus 18 in which objectionable

\* U. S. Patent No. 1,167,915, January 11, 1916.

matters are separated from the gas and from which the purified gas is returned to the gas holder 13, to which fresh gas is supplied as may be necessary. Circulation of the gas through the apparatus is maintained by a pump 27. The inclined tube or conduit is heated to a reducing temperature. When diatomaceous earth impregnated with nickel hydroxide is treated, a temperature of about 550° F. is preferred. The treating tube may be inclined at such an angle, usually about 42°, that the material will flow through the tube by gravity, or as shown in the illustration, the tube may be inclined at a less angle and a jarring or shaking mechanism be provided for causing the material to flow properly. As shown, the carrying frame for the tube is movably supported by a hinge at its lower end and rests at its upper end upon a rotating cam.

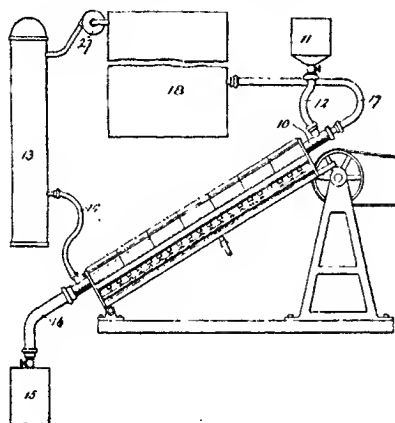


FIG. 47c.

To suppress the tendency of catalytic materials to heat or take fire on exposure to oxygen, air or other gases containing oxygen, **Morey** \* exposes the catalytic material to a partial vacuum for a sufficient length of time to practically remove the occluded gas which is absorbed by or associated with the particles of catalytic material.

Exposure to a partial vacuum, as complete as circumstances will permit and maintained for a sufficient length of time, renders the catalytic substance practically free from occluded gas and capable of being exposed to air without developing undesirable pyrophoric action. This method can be applied to the various catalytic metals, such as finely-divided nickel, cobalt or platinum. The catalytic material is placed in an air-tight vessel which is connected with a vacuum pump. The latter can be operated continuously or intermittently. The vacuum vessel may be heated. A satisfactory practice is to operate the pump until the partial vacuum in the vessel has attained the limit which the pump can produce. The vessel is then sealed by closing a stop cock in the passage

\* U. S. Patent No. 1,127,911, February 9, 1915.

leading to the pump. The catalyzer is allowed to remain under this reduced pressure for about twelve hours, during which time the occluded gas gradually leaves the catalyzer and the latter becomes practically non-pyrophoric. If desired, however, the period of rest may be shortened to about three hours and the pump be operated again to remove as far as practicable the gas which has become liberated during the period of rest, and this second operation of the pump may be followed by another period of rest. An inert gas, for instance, nitrogen, may be admitted to the vacuum vessel at the end of the period of rest and the vessel again exhausted. The gas so admitted to the vacuum vessel mingles with the liberated gas in the vessel and is said to facilitate the removal of the rest of the occluded or liberated gas. The desired non-pyrophoric condition has been produced when a sample of the material under treatment does not heat when exposed to the atmosphere.

A nickel catalyst for use in hydrogenating oils is prepared by **Morey and Craine**\* in the following manner:

An insoluble nickel compound such as the hydroxide, and fuller's earth, are suspended together in water (after heating the fuller's earth sufficiently to drive off moisture and gases from it) and the intimately associated mixture of nickel hydroxide and fuller's earth thus obtained is dried, comminuted and reduced with hydrogen to form a catalyst suitable for hydrogenating oils or fats. For example, 60 parts of nickel sulphate may be used to prepare the hydroxide which is mixed with 25 parts of fuller's earth.

A process of making a nickel catalyst is described by **Burchenal**,† according to which, sulphate of nickel is dissolved in water and sodium carbonate added to precipitate nickel carbonate, which is washed, dried and calcined to eliminate carbon dioxide and thereby form an oxide. This product is reduced to finely-divided nickel by heating in a current of hydrogen. To render the product non-pyrophoric, it may be cooled in an atmosphere of hydrogen or carbon dioxide. The nickel is used without a carrier in the hydrogenation of unsaturated fatty acids or their esters.

The protection of a pyrophoric catalyst by incorporation with fatty material is described by **Oswald and Doering**,‡ who consider hardened oil a desirable protective agent.

The product is prepared simply by mixing any suitable catalyst of a pyrophoric nature, without access of air, with the fatty material in a melted condition, if the latter is solid at ordinary temperature, then permitting the whole, while being agitated, to cool to a point just above its melting-point, when the whole mass is poured into any convenient receptacle for use, storage or shipment. Or the finely-distributed freshly-reduced unused metal is introduced into a vessel containing such fat in a liquid state and under an atmosphere of hydrogen and the whole permitted, while being agitated, to cool. The fat with which the

\* U. S. Patent No. 1,232,830, July 10, 1917; J. S. C. I., 1917, 1039.

† U. S. Patent No. 1,226,945, May 22, 1917.

‡ U. S. Patent No. 1,187,775, June 20, 1916.

finely-distributed active metal is incorporated acts as a protective and shielding agent. The quantity of fat used may vary within considerable limits, equal parts of the agent and fat making a satisfactory article. With about equal amounts of readily solidifying fat and catalytic agent, this result is obtained and an article of desirable consistency, readily handled, and subdivided is obtained. It carries a substantial amount of catalyst; an amount sufficient for the treatment of many times the amount of oil or fat it contains. On placing it in hot oil, the fat melts and dissolves; and if it be of the same nature as the fat to be produced from such oil, its presence does not change in any way the nature of the final product. In any event, the amount which is used with the agent is, relative to the amount of oil which can be treated with a given amount of agent, wholly insignificant.

Colloidal nickel or other colloidal metal catalyzer may be advantageously sealed in hydrogenated oil.\*

The handling and shipment of catalytic material in a special manner is described by Sulzberger.†

A catalyst, for instance, such as is obtained by rendering nickel silicate catalytically active by subjecting to reduction by means of hydrogen, after such reduction is immediately cooled while still in the atmosphere of the hydrogen, and covered with hydrogenated cottonseed oil, which will solidify to a solid mass. In this condition the catalyst can be kept as well as shipped to points for its use. The homogeneous nature of the product makes it possible to procure desired quantities of the nickel-catalyst by simply weighing off amounts of the mass or taking pieces of certain size and bulk. The mass may contain lines or markings, from which the amounts of catalyst contained in pieces of certain size may be judged, so as to make weighing off of desired quantities unnecessary. The mass may also be formed in individual pieces (cubes, tablets, balls, etc.) containing definite amounts of the catalytic agent.

#### CATALYZER POISONS

Sabatier and Espil ‡ have concluded that the effect of sulphur and the halogens as catalyzer poisons has been exaggerated.

Traces of these substances do not appear sufficient to destroy the activity of nickel. For example benzene containing 0.5 per cent iodine in solution was completely transformed into cyclohexane. The nickel in about one-half of the hydrogenating tube toward the inlet side was affected but the catalyzer in the other half of the tube remained active. Chlorine and bromine, introduced as hydrochloric or hydrobromic acids or as halogenated benzol, also sulphur in the form of carbon bisulphide, acted in a similar manner. Moreover the nickel which is rendered inactive to benzol still preserves the power of carrying hydrogen to nitrils and other aliphatic or aromatic organic compounds but is incapable of hydrogenating ketones or ethylene hydrocarbons. Sabatier and Espil recommend that nickel poisoned by chlorine be revived by using it to hydrogenate

\* Ellis, U. S. Patent 1,226,620, May 15, 1917; Reissue 14,429, Jan. 29, 1918.

† U. S. Patent No. 1,223,123, April 17, 1917.

‡ Bull. Soc. Chim., Vol. XV., 1914, 778.

nitrobenzene. After a few hours use in this manner the catalyzer is reactivated and will convert benzene into cyclohexane. When poisoned by bromine or iodine this treatment is not effective.

Potassium cyanide was found by Peters\* to poison palladium catalyzer.

A method of removing catalyzer poisons from oil, recommended by the author† is to treat the oil with catalyzer which has lost its catalytic activity.

To this end a finely-divided spent nickel catalyzer is vigorously agitated with the oil at a temperature of about 180° C. until catalyzer poisons have been absorbed when the oil is filtered, fresh catalyzer added and hydrogenation is completed. The treatment of the oil depends upon the character of the catalyzer poisons present. Aluminum, nickel, copper, etc., and their basic compounds in a finely-divided state can be used.

One of the main difficulties in the hydrogenation, by the aid of nickel catalyzer, of many low-grade oils, such as some of the fish and whale oils, is that the life of the catalyzer is relatively very short. Ellis and Wells‡ have studied the problem of treating such oils to adapt them to the hydrogenation process.

Usually the activity of the catalyzer becomes much slower after two or three batches of oil have been hardened and in some cases it is necessary to prepare fresh catalyzer for every batch of oil treated. On the other hand, when hardening a good grade of oil, such as refined, edible cottonseed oil, the life of a carefully prepared catalyzer is likely to be very long and in some cases an entirely new lot of catalyzer is not required for months in the constant operation of a hardening plant. In these cases the catalyzer is kept in a state of high activity for continued usage by adding a small amount of fresh catalyzer at intervals of one or two weeks. It has been observed that some kinds or grades of oil may be hydrogenated to an incomplete degree but that they cannot be carried beyond this point, no matter how long the treatment is continued, without change of catalyzer. If to these semi-hardened oils a fresh quantity of catalyzer is added the hardening will usually proceed practically to complete saturation. In some cases, a fresh quantity of oil may be treated with the seemingly spent catalyzer, when partial hardening will occur. An additional quantity of fresh catalyzer will sometimes carry the oil so treated, to completion, showing that the substance which affects the catalyzer is apparently taken up by it under these circumstances, thus leaving the oil in condition to be readily hardened. Some oils which ordinarily cannot be hardened without a preliminary purifying treatment, may first be agitated with a spent catalyzer, the catalyzer removed and the oil then incorporated with a fresh quantity of catalyzer when hardening readily occurs.

\* Inaugural Dissertation, Leipsic, 1913.

† U. S. Patent No. 1,132,710, March 23, 1915.

‡ J. Ind. Eng. Chem., 1916, 886. See also U. S. Patent to Ellis, 1,247,516, Nov. 20, 1917.



**Cod Oil.** Crude cod oil was freed from fatty acids with a solution of sodium carbonate and after washing free from alkali and soap was treated with hydrogen, using 5 per cent catalyzer prepared from nickel oxide. In several trials, the oil either did not harden at all, or only to a very minor degree. Other forms of catalyzer were equally ineffective. The oil was then agitated for one hour at 200° C. with freshly-prepared copper hydrate, filtered to remove the copper compound and again treated with hydrogen and catalyzer under the same conditions as above. The oil was readily hardened by this treatment. Another sample of the oil, refined as above, was treated with 5 per cent freshly-prepared silver oxide at 200° C. for one hour. The silver compound was removed by filtration and the clear oil hydrogenated. In a short time this oil was hardened to a melting-point of 46° C. on hydrogenating under the same conditions as above.

A series of tests were performed to determine the relative value of freshly-precipitated copper hydrate as a detoxicating agent. In one test, portions of cod oil were agitated with 5 per cent of freshly-prepared copper hydrate, commercial copper carbonate and lead oxide at 180° to 200° C. for two hours. After filtering, these samples were treated with hydrogen using 5 per cent nickel oxide as a source of catalyzer. This was reduced in oil at 250° C. for one-half hour. The hydrogenation operation was carried out at 230° C. for three hours. The oil treated with freshly-precipitated copper hydrate hardened to a melting-point of 53° to 54° C., the oil treated with copper carbonate hardened slightly, while the oil treated with lead oxide did not harden.

To determine the most effective temperature for treating the oil with copper hydrate the following tests were performed: Cod oil was agitated with  $\frac{1}{2}$  per cent of copper hydrate for one hour at room temperature, then was filtered and subjected to the hydrogenation process. Another portion of the oil was treated in a similar manner, except the temperature of treatment with copper hydrate was 50° C. Other portions were treated at 75° and at 110° to 120° C. The samples treated below 110° C. did not harden and metallic mirrors were formed on the walls of the container during the treatment with hydrogen. The sample which was agitated at room temperature exhibited the most perfect mirror. The oil treated at 110° to 120° C. hardened readily without the formation of a mirror.

The effect of refining cod oil with alkali before hydrogenation, when the copper hydrate treatment is used, is beneficial to the catalyzer as was shown by agitating crude cod oil with copper hydrate at 140° to 150° C. for one hour, filtering and then subjecting it to the hydrogenation process, using nickel oxide. The catalyzer was formed in the oil at 250° C. and hydrogenation was carried out at 190° to 200° C. for four hours. The oil was only slightly hardened.

A quantity of the oil under examination was burned in oxygen in a combustion bomb. The contents of the bomb were washed out and examined qualitatively. Sulphates and a trace of iodine compounds were found to be present but no test was obtained for either chlorides or phosphates. Either sulphur in the sulphide form, or iodine could have been responsible for the poisoning action on the catalyzer noted.

**Manhaden Oil.** Southern crude fish (menhaden) oil, without refining, was subjected to the hydrogenation process, using nickel oxide reduced in the oil at 250° C. and the hydrogen treatment was carried out at 200° C. for four hours. The oil was not hardened. Another portion of the same oil was agitated with copper hydrate at 135° to 150° C. for one hour and treated under the same con-

ditions as above. The oil was hardened, without difficulty, to a melting-point of 45° to 46° C. Another quantity of the same crude fish oil was refined and then treated with copper hydrate. The treated oil was hydrogenated using a catalyzer which had previously been used in cod oil that had been detoxicated with copper hydrate. The oil hardened to a melting-point of 52° to 53° C. The catalyzer was apparently not affected by its previous use in cod oil which had been treated with copper hydrate.

Herring oil which could not be hardened by the usual methods was refined to free it from fatty acids and after treating with copper hydrate for one hour at 110° to 120° C. was subjected to the action of hydrogen in the presence of a catalyzer prepared by reducing nickel oxide in the oil at 250° C. for one-half hour. The oil was hydrogenated at 190° to 200° C. for five hours. It hardened to a melting-point of 45° to 46° C.

Dogfish Oil. This oil has proved somewhat difficult to hydrogenate. In one case, a sample of the oil was agitated with copper hydrate for one hour and then treated with hydrogen, using a catalyzer prepared by precipitating nickel hydrate on a carrier and reducing at 360° C. Hydrogenation was conducted for 5½ hours at 180° to 190° C. The oil did not harden. The catalyzer was filtered out and 5 per cent of a mixture of finely-divided nickel-copper hydrate was added. A current of hydrogen was passed through the oil, the temperature of the oil being held at 250° C. for one-half hour, then lowered to 190° to 200° C. and maintained at that point for three hours. The oil hardened to a melting-point of 45° C.

It has generally been assumed that the presence of sulphates in a nickel catalyzer is prejudicial but repeated tests by the author have shown this not to be the case under certain conditions. If the sulphate is of a difficultly reducible character as, for example, sodium sulphate, the nickel is practically unaffected, especially if the reduction has taken place at a relatively low temperature. When a mixture of nickel hydrate or carbonate and sodium sulphate is reduced at a temperature somewhat below 250° C. the activity of the catalytic nickel is not materially affected by the sulphate. Apparently sulphur in the sulphide form is necessary in order to poison the catalyzer. Catalytic material containing sulphates has been employed on a commercial scale in this country for a considerable period of time with satisfactory results.

The effect of sulphur and arsenic in hydrogen gas employed for oil hardening has been investigated by Hehner and reported by Crossley.\* Curves of absorption were obtained which indicate the deleterious action of arsenic and sulphur. Unpurified hydrogen such as was obtained from a good specimen of zinc and acid did not permit the catalyzer to function as actively as in the case of pure hydrogen. When hydrogen was passed through a very dilute solution of hydrogen sulphide in water the effect on the catalyzer was very marked. The effect of using crude water gas containing about 28 per cent of hydrogen in comparison with water gas which

\* Pharm. Soc. April 21, 1914; Pharm. J. 1914, 92, 604, 637 and 676; J. S. C. I., 1914, 1135.

Carbon bisulphide: (a) 0.0005 g., 25 per cent; 0.003 g., 0 per cent. (b) 0.003 g., 60 per cent; 0.01 g., 1 per cent. (c) 0.01 g., 63 per cent; 0.06 g., 3 per cent. Practically all of the sulphur found (corresponding to about 50 per cent of that in the carbon bisulphide used) was in the solid nickel as sulphide, with only traces in the filtrate.

The effect of catalyzer poisons has also been studied by **Moore, Richter and Van Arsdel**.<sup>\*</sup> The experiments on poisons were carried out in an apparatus containing oil and catalyzer, through which hydrogen was bubbled. A mixture of oil with 1 per cent nickel on a carrier was hydrogenated first for one hour to ascertain the original activity of the catalyzer. At the end of the hour, 2 per cent of the finely powdered solid substance in question was added, and the hydrogenation continued. Samples were then taken at intervals to determine the further fall of the iodine number, and the poisoning effect was judged by the shape of the iodine number-time curve, compared to one in which no poison was present. The results may be summarized as follows:

Substance.	Effect on Activity.
Sulphur.....	Destroyed immediately
$\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ .....	Gradually destroyed
$\text{NaCl}$ .....	No effect
$\text{Na}_2\text{SO}_4$ .....	No effect
$\text{NaNO}_3$ .....	No effect
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ .....	No effect
Reduced iron.....	No effect

The three gases  $\text{H}_2\text{S}$ ,  $\text{SO}_2$  and  $\text{Cl}_2$  were also tried. In each case the activity was destroyed immediately. A small amount of water vapor in the hydrogen was found gradually to destroy the activity of the catalyzer.

Concerning the phenomena of catalytic poisons, **Bancroft** † remarks that the adsorption of reacting substances and consequently reaction velocity are decreased by the presence on the solid catalytic agent, of a film of solid, liquid, or gas. Very small amounts of grease will keep palladium from taking up hydrogen. Carbon monoxide may act as a catalytic poison by decreasing the adsorption of other substances. It is very tenaciously held by platinum. Reaction products may decrease reaction velocity by hindering diffusion of reacting substances to the catalytic agent and by decreasing their adsorption.

The work of **Marted** ‡ indicates carbon monoxide to retard the

<sup>\*</sup> J. Ind. Eng. Chem., 1917, 451.

† J. Phys. Chem., 1917, 21, 734; Chem. Abs., 1918, 12, 328.

‡ Trans. Faraday Soc., 1917 (advance copy); Chem. Trade J. 61, 509-10.

rate of addition of hydrogen to fatty oils. The inhibitive effect of carbon monoxide was studied from a quantitative standpoint for the hydrogenation of olive oil using finely-divided nickel as catalyst. The experiments were carried out with 10 g. of oil and 0.1 g. of nickel, using pure hydrogen, and hydrogen containing 0.25, 0.5, 1.0 and 2 per cent of carbon monoxide respectively. The absorption was noted at five-minute intervals for one hour, at the end of which pure hydrogen showed 584.5 cc. absorption, hydrogen containing 0.25 per cent carbon monoxide, 393.9 cc.; hydrogen containing 0.5 per cent, 309.6 cc.; hydrogen containing 1.0 per cent, 235.2 cc.; and hydrogen containing 2 per cent, 158.8 cc. Maxted considers these results to show a marked poisoning influence by carbon monoxide, an effect which was differentiated from the calculated obstructive effects of the impurity. The first traces of carbon monoxide have relatively the greatest retarding influence on the velocity of hydrogenation.

Pierron \* gives a lengthy description of an ignition catalyst having the following properties. "A porous or finely-divided matter or product (or mixture of products) constituting in some manner a support serving to prevent agglomeration of the second product. This matter or product or mixture of matters or products is termed the supporting element." The catalytic agent employed is platinum, palladium or similar rare metal, supported on an oxide of silicon, aluminum, iron, manganese, etc.

Hagemann and Baskerville carry out hydrogenation by means of a catalyzer of nickel sheet, wire or other nickel "shapes" having a coherent layer of nickel oxide closely adhering to the metal surface.† In using these "oxide-tarnished" metal shapes, hardened fats are said to be obtained in a remarkably clean undiscolored state.

\* Elworthy ‡ states that copper or other metals as wire or sheets coated with nickel may be used as catalytic material.

An organosol adapted for use as a catalyst in fat hardening is prepared by Karplus § as follows:

An irreversible colloid is removed from a hydrosol by producing within the latter an amorphous organic precipitate which is soluble in the organic substance in which it is desired to produce the organosol. The precipitate is separated, heated to remove water, and then mixed with the organic substance, when an organosol of the desired colloid is obtained.

\* British Patent No. 15,414 of 1898.

† U. S. Patent No. 1,238,137, August 28, 1917.

‡ U. S. Patent No. 943,627, Dec. 14, 1909.

§ J. S. C. I., 1916, 823; British Patent No. 8,641, June 11, 1915; German Patent No. 293,848, November 13, 1913.

has passed through soda line is shown by Hehner. The purified water gas permitted catalytic action to go on to better advantage.

**EFFECT OF HALOGENS, HALOGEN COMPOUNDS, SULPHUR, ETC.,  
ON HYDROGENATION OF COTTONSEED OIL \***

CATALYZER: NICKEL OXIDE (5 PER CENT OF THE WEIGHT OF THE OIL) REDUCED  
IN OIL AT 250° C. FOR ONE-HALF HOUR

Expt. No.	Substance Added.	Per cent Added	Temp., ° C.	Time, Hours	Effect on Oil
1	Bromine.....	1.0	200	2	No hardening
1 (CH)		1.0	200	2	
2	Iodine.....	1.0	200	2	
2 (CH)		1.0	200	2	
3		0.5	200	2½	
3 (CH)		0.5	200	2½	
4	Antimony Bromide	1.0	200	2	
4 (CH)		1.0	200	2	
5	Sodium Chloride .	5.0	210	2½	Oil hardened
6	Zinc chloride.....	5.0	210	2½	Oil polymerized
7		1.0	200	2½	Slight hardening
7 (CH)		1.0	200	2½	Oil hardened
8		0.5	200	2½	
9	Tin chloride.....	1.0	200	2	
10	Sulphur.....	0.5	200	2½	Slight hardening
10 (CH)		0.5	200	2½	Oil hardened
11		1.0	200	2½	No hardening
11 (CH)		1.0	200	2½	Oil hardened
Blank		.....	200	2½	
12	Sulphur .....	0.1	210	3½	
13	Red phosphorus.....	1.0	200	2	Slight hardening
13 (CH)		1.0	200	2	Oil hardened
14		0.5	200	2	Slight hardening
14 (CH)		0.5	200	2	Oil hardened
15	Sulphur chloride.....	1.0	200	2	No hardening
15 (CH)		1.0	200	2	Oil hardened
16	(As <sub>2</sub> O <sub>3</sub> ).....	1.0	200	2	No hardening
17	Mercury.....	1.0	200	2	Slight hardening
Blank		.....	200	2½	Oil hardened
18	Lead stearate.....	1.0	200	2½	No hardening
19	Lead oleate.....	1.0	200	2½	
19 (CH)		1.0	200	2½	

(CH) after an experiment number indicates treatment with copper hydrate before hydrogenation.

**Kelber** † has found that nickel catalyzers made in different ways behave entirely differently, in reducing reactions, toward contact

\* Ellis and Wells, J. Ind. Eng. Chem., 1916, 886. † Ber. 49, 1868.

poisons such as hydrocyanic acid or potassium cyanide, hydrogen sulphide and carbon bisulphide.

The following catalyzers (a) from basic nickel carbonate reduced at 450° in hydrogen (b) from basic nickel carbonate reduced in hydrogen at 310° and (c) from basic nickel carbonate on inorganic carriers reduced in hydrogen at 450°, show a sensitiveness to these poisons, decreasing in the order (a), (b) and (c). This is believed to be due to the fact that the high temperature at which (a) is prepared changes the surface of the individual particles of the catalyzer so that there remain only a few points on these particles which are capable of adding hydrogen and acting as a carrier of it, and these points, being more reactive than the rest of the nickel are the first to act on the poison, so that relatively small amounts of the latter are able to poison the whole of the catalyzer. The lower temperature used in preparing (b) leaves more of these active spots, while in (c) the presence of the inorganic skeleton doubtless hinders the change in the surface of the catalyzer. The experiments were carried out at room temperature under atmospheric pressure in a shaking apparatus, 0.5 g. of the metal being shaken twenty minutes with the poison in 25 cc. water in a hydrogen atmosphere, then treated with  $C_6H_5CH:CHCO_2Na$  (0.75 g. acid and somewhat more than the calculated amount of caustic soda in 25 cc. water) and the absorption of hydrogen measured every five minutes. Below are given the per cent of its original value to which the reducing power of the 3 catalyzers is decreased by varying amounts of the different substances in the first fifteen minutes. Potassium cyanide: (a) 0.00005 g., 45 per cent; 0.0003 g., 2 per cent; (b) 0.0003 g., 55 per cent; 0.001 g., 0 per cent. (c), 0.002 g., 25 per cent; 0.02 g., 2 per cent. (It is not clear in the original whether the amounts given above represent the weights of potassium cyanide used or the amounts of hydrocyanic acid equivalent to the salt used.) Hydrocyanic acid: (a) 0.0005 g., 63 per cent; 0.002 g., 1 per cent. (b), 0.001 g., 50 per cent; 0.005 g., 0 per cent. Traces of alkalis give entirely different values and as (c) could not be entirely freed of alkalis it was not used in this series. The small "toxicity" of hydrocyanic acid as compared with potassium cyanide is ascribed to the rapid change of hydrocyanic acid in the presence of nickel and hydrogen; the catalyzers poisoned with hydrocyanic acid retain only traces of the poison, whereas with potassium cyanide, the catalyzer shows large amounts of the poison, although in a changed form. To test the effect of hydrocyanic acid, potassium cyanide and nickel cyanide on the catalyzer, (b), after saturation with hydrogen was shaken in hydrogen to constancy of volume with definite amounts of solutions of the 3 substances, filtered and the poison determined in the solid and the filtrate; the filtrate was found to be free from hydrocyanic acid but to be strongly alkaline and contain ammonia, probably produced by a catalytic reduction of hydrocyanic acid or a nickel cyanide compound, as several cc. of hydrogen were always used up; the solid nickel, when dissolved in sulphuric acid and heated with alkali, gave a distillate containing ammonia; no amines, or only traces at most, were found in the solid or filtrate. A catalyzer poisoned with potassium cyanide, then filtered and washed with water, does not recover its activity, but this can be restored by treating once with hydrogen and warming with ammonia, or, best, by boiling with caustic soda.

Hydrogen sulphide: (a) 0.001 g., 25 per cent; 0.005 g., 1 per cent. (b) 0.01 g., 15 per cent; 0.02 g., 0 per cent. (c) 0.02 g., 60 per cent; 0.1 g., 0 per cent. The sulphur is found almost entirely as sulphide, in the solid nickel.

The addition of substances, refractory at the required temperature and chemically inactive towards the mixture, to increase the efficiency and the period of activity of contact masses and to avoid the possibility of a reaction between the catalyst and the constituents of the support of the contact material is detailed by **Nitrogen Ges. m.b.H.\*** For example, in the use of a mixture of copper and copper oxide as the catalyst, and clay or other materials containing silicates as the support, the addition of aluminium oxide causes the mass to retain its activity for a longer period. The reaction between the copper oxide and the silicates is prevented and the catalyst is so finely distributed throughout the mixture that the agglomeration or fusion of copper cannot take place. The mass is stated to possess a high degree of porosity.

For the reduction of oils with hydrogen under a pressure of nine atmospheres, an apparatus was constructed by **Hamburger,†** resembling the one described by Stuckert and Enderli.‡ The influence of temperature, pressure, divisibility of the catalyst, and kind of oil (impurities therein) on the hydrogenation process was investigated. The hydrogenation of all pure oils with finely-divided nickel, as a catalyst, proceeds without difficulty; the same holds true for fatty acids obtained from very impure oils by distillation, with steam vacuo. The nickel catalyst was obtained by the reduction at 260° to 300° of nickel oxide, which had been previously precipitated on pumice stone. It appears, according to Hamburger, that tungsten, molybdenum, thorium, uranium, zirconium, titanium, vanadium and manganese cannot be used as catalysts in the hydrogenation of oils. He states that the claims by the author § could not be confirmed, not even when a hydrogen pressure of 200 atmospheres was applied.||

Aromatic amines are obtained by a process of the **Badische Co.¶** by reduction of nitro compounds, with hydrogen, water gas, etc., in contact with a catalyst consisting of copper made by reducing at a temperature below red heat copper oxide prepared otherwise than pyrogenetically, together with a promoting agent; precipitation of copper salts by means of caustic soda is a suitable method of forming the oxide. According to examples, a paste of coarse pumice, copper oxide, zinc carbonate and water is reduced by water gas, and then a mixture of

\* French Patent No. 453,099, January 13, 1913; J. S. C. I., 1913, 741.

† Chem. Weekblad, 13, 2-13, 1916; Chem. Abs., 1916, 826.

‡ A bomb provided with a stirrer for the intimate mixing of a liquid and gas under high pressure and temperature, designed to keep the liquid saturated with the gas as the reaction proceeds. A form of valve for reducing pressures is also described. (Z. Electrochem., 19, 570.)

§ U. S. Patent No. 1,026,156.

|| The observations of Hamburger are not in agreement with the results of other investigators. A number of the bodies described by Hamburger as having no catalytic properties have been found to serve as activators or co-catalysts in conjunction with nickel and the like.

¶ British Patent No. 5,602, April 15, 1915.

a nitro compound and water gas is passed over the reduced mass; a paste of pumice in lumps, copper hydrate, silver oxide, water-glass and water is prepared and is reduced by hydrogen and then a mixture of vapor of nitro compound and hydrogen is passed over the reduced mass; a solution of copper, silver and magnesium nitrates is precipitated with caustic soda, the washed precipitate is made into a paste with pumice in lumps, water-glass and water and is then reduced by hydrogen. A mixture of a nitro compound and hydrogen is passed over the reduced mass.

Walter (Soc. L'Oxylythe) \* facilitates separation of the catalytic agent after the hydrogenation by employing catalysts which are either magnetic in themselves, or may be rendered temporarily magnetic after the reaction, or rest upon magnetic supports, and, therefore may be retained within the vessel by subjecting this to the action of a magnetic field when the hydrogenated product is withdrawn. Various devices for carrying out the process are described.

Reynolds † notes that the danger of explosion when using hydrogen to reduce catalytic raw material is a serious menace because the reduction of the material being treated is usually effected in a drum or cylinder that is heated by a flame and the slightest defect in the drum would permit the escape of hydrogen into the flame with disastrous results.

Instead of hydrogen, Reynolds finds ammonia may be used, or even carbon monoxide if rendered non-inflammable by admixture with an inert gas. Also it is possible to mix hydrogen with inert gas so that it is rendered non-explosive. This inert gas may be either carbon dioxide or nitrogen or a mixture of both, their proportions being immaterial so long as the percentage of reducing gas does not reach the explosive point. Reynolds states that even 5 per cent is non-explosive. He thinks that the inert gas appears to envelop the reducing gas in the mixture so that it is rendered non-explosive but does not combine with it to change its reducing quality in any degree. While ammonia may be used alone, it may be also mixed with the inert gas. The preferred mixture is nitrogen, carbon dioxide and carbon monoxide and a method of making it is to draw air through burning coke in a closed container; washing the resulting product and then conducting it into the reducing drum. The air after passing over the coke becomes a mixture of gases containing approximately 78 per cent nitrogen, 20 per cent carbon dioxide, and a 2 per cent carbon monoxide. This mixture is stated to be efficient as a reducing agent, is cheap to make and is non-explosive. The resulting catalyst may be exposed to the atmosphere for about thirty minutes without detriment to its catalytic properties.

To prepare an unsintered nickel powder by dry reduction, Ellis ‡ prepares a reducible nickel salt or basic compound such as the car-

\* French Patent No. 471,108, April 18, 1914; J. S. C. I., 1915, 162; Seifen. Ztg., 1915, 309.

† U. S. Patent 1,210,367, December 26, 1916.

‡ U. S. Patent No. 1,185,075, May 30, 1916.



bonate, hydrate or oxide in a finely-divided condition as by precipitation.

For example, nickel nitrate is precipitated with ammonia and dried with some of the ammonium nitrate formed by the reaction present in the precipitate. When dry the product is well washed and finely-divided nickel hydrate in a substantially uncontracted precipitated form is obtained. This may then be reduced with hydrogen under normal atmospheric pressure at the temperature of say 200° to 300° C., until part of the oxygen is removed. The partially reduced product is then subjected to hydrogen under a pressure of about four or five atmospheres while maintaining the temperature at approximately the same point. By the application of the hydrogen under pressure, reduction to a product consisting almost solely of finely-divided metallic nickel takes place without running up the temperature to a point where catalytic sensitiveness is lost by contraction of the particles as a result of sintering or fritting due to excessive temperatures.

In an article on catalysis by Leimdorfer\* it is stated that by reducing a body to a fine powder thereby increasing the surface, new properties and new powers are acquired; as for example, by finely dividing metals the pyrophoric condition is obtained.†

The separation of nickel and cobalt from aqueous solutions of their salts by hydrogen at high temperatures and pressures has been studied by Ipatiew and Zvjagin.‡

An investigation of the displacement of cobalt, from aqueous solutions of its sulphate, nitrate and chloride by hydrogen at high temperatures and pressures, shows that such similar metals as nickel and cobalt give in this way substances of different properties, although the general character of the phenomena is the same as with copper and nickel salts.§ Cobalt salts show a number of independent reactions, which depend on critical temperatures and pressures and give rise to separation of basic salts, the oxide of the metal, and finally, the metal itself.

The temperature of decomposition of copper nitrate has been determined by Rolla.||

A mixture of nitrogen dioxide (NO<sub>2</sub>) and oxygen, obtained by the decomposition of lead nitrate, was led over a weighed quantity of copper oxide at temperatures of from 70° to 300° C. At 250° C. and higher temperatures, the copper oxide showed no gain in weight, and hence the temperature of complete decomposition of copper nitrate at atmospheric pressure is given as 250° C.

**The Naamloose Vennootschap Ant. Jurgens Vereenigde Fabrieken** regenerate metallic catalyzers by burning off the organic

\* Seifen. Zeitung, 1914, 1345.

† See also Seifen. Zeitung, 1914, 1253, 1276, 1298, 1323; 1915, 303.

‡ J. Russ. Phys. Chem. Soc., 1912, 44, 1712-1715; J. S. C. I., 1913, 84.

§ J. S. C. I., 1911, 900.

|| Gas. Chimp. Ital., 1915, 45, 1, 444-450; J. S. C. I., 1915, 796.

material, when the catalyzer can be used immediately or after reduction in a current of hydrogen.\*

The regeneration of nickel catalysts is carried out by the *Soc. Industrielle de Produits Chimiques*,† by wholly or partially removing adherent organic matter, as by solution and then heating the residue while stirring with access of air. The product may be washed with water and again heated to redness. It is then ready for use as oxide; or the oxide may be reduced to suboxide by heating to about 300° with about its own weight of oil in a current of hydrogen. A catalyst consisting of metallic nickel may be obtained by reducing at a low temperature the nickel oxide catalyst described above or heating the original spent catalyst wholly or practically freed from organic matter, without access of air or in presence of a reducing agent.

For the preparation of reduced nickel Lane‡ employs a circular air-tight pan provided with a vertical shaft carrying two arms which are curved helically in a horizontal plane. The arms carry sliding teeth which rest on the bottom of the pan, and the shaft may be rotated in either direction so that the material in the pan may be forced outwards or inwards as desired. The raw material is fed into the pan from a valved hopper, a reducing gas is introduced and heat is applied till water ceases to be evolved. The rotation of the shaft is then reversed, and the material is thereby collected towards the centre of the pan and discharged into a well or seal containing oil.

To convert finely divided metals reduced from their oxides by hydrogen, into a non-pyrophoric condition Edison§ employs a current of nitrogen or other inert gas to displace the hydrogen. On removal of the hydrogen in this manner the metal may be exposed to the air without danger of spontaneous oxidation.

Schwarzman|| employs a catalyzer of nickel incorporated with precipitated alumina or supported on a carrier of fuller's earth, there being present a nitrogenous organic colloid such as wool. For example, 1 part fuller's earth is suspended in 5 parts of a 15 per cent caustic soda solution and boiled for one hour. The earth is then washed, placed in 10 parts of water and 1 part of nickel nitrate in 3 parts of water is added. After boiling, 275 parts of caustic soda and .2 parts wool dissolved in 2.5 parts water are introduced. The earth and precipitate is pressed, dried and reduced in hydrogen.

Kimura¶ heats a nickel salt on a carrier of asbestos or pumice, in an atmosphere of ammonia gas or a vaporized ammonium compound, such as ammonium chloride. The catalytic material so prepared is stated to be active at a relatively low temperature.

\* Chem. Abs., 1914, 3356; French Patent No. 465,256, November 24, 1913.

† British Patent No. 111,840, November 5, 1917.

‡ British Patent 115,924, June 11, 1917; J. S. C. I., 1918, 397 A.

§ U. S. Patent 1,275,232, August 13, 1918.

|| U. S. Patents 1,172,062, February 15, 1916; 1,280,314, October 1, 1918. Also note 1,111,502, September 22, 1914.

¶ J. S. C. I., 1918, 594 A; British Patent 118,323, August 22, 1917.

## CHAPTER VII

### THE BASE METALS AS CATALYZERS—Continued

Wesson \* prepares a catalyzer by first dissolving nickel nitrate in water and then adding ammonium hydrate, which causes nickel hydrate to be precipitated in the form of a voluminous, flocculent precipitate.

Care should be taken to add only a sufficient quantity of ammonium hydrate to form the precipitate, as an excess will break down the hydrate of nickel and cause it to re-dissolve. In thus using ammonia as a precipitant, sulphates or chlorides which may be present in the nickel nitrate will be converted into sulphates or chlorides of ammonium and these are volatilized at the temperature at which the nickel is subsequently reduced. This serves as a method of purification, which is very desirable in order to produce an active catalyzer. After the precipitate of hydrate of nickel is formed, the supernatant liquid containing ammonium nitrate and some unprecipitated nickel salts may be decanted off, leaving nickel hydrate and water with a small amount of ammonium salts dissolved in the water. This flocculent precipitate is then mixed with the inert carrier to which it is to be applied, as, for instance, asbestos. The precipitate and the support are then dried to expel the water and are heated at a temperature of say 500° C. in a current of hydrogen until the nickel has been reduced to a finely-divided condition, covering the asbestos fibers or other support used. The ammonium nitrate that remained in the water assists in this. As the support covered by the flocculent precipitate is heated, the ammonium nitrate is decomposed, leaving most of the nickel hydrate around it in a very fine and spongy condition, in which form it is more easily reduced by the hydrogen, and at the same time the operation puts it in such shape as to present a greater surface for contact action.

There are stated to be substantial advantages in applying the flocculent hydrate of nickel to the support, instead of applying to the support a solution of a salt and afterward adding a precipitant. For in the former case the hydrate acts only on the surface of the support (which is the place where it is wanted) and is not soaked up into the internal pores of the support, as it would be if the support were treated with a solution of a salt and precipitation were brought about afterward.

Nickel hydrate such as used in the foregoing (Wesson) catalyzer is prepared according to Woodruff,† in the following manner:

Nitrate of nickel or other nickel oxygen salt is dissolved in sufficient water to form a dilute solution, which should contain about 1 per cent of the crystalline

\* U. S. Patent No. 1,143,339, June 15, 1915.

† U. S. Patent No. 1,143,343, June 15, 1915.

salt, and the solution is then brought to a temperature in the neighborhood of the boiling-point. Satisfactory results are obtained at a temperature of approximately 95° C. Sufficient hydroxide of ammonium to theoretically precipitate all the nickel present is then added. In practice an ammonium hydroxide solution of a specific gravity of about 26° Baumé is used. The correct amount of a given solution of the ammonium hydroxide to add to the solution of the nickel salt may be determined by slowly adding the ammonia to a small quantity of the nickel solution under the above conditions, and noting the point at which the precipitate commences to dissolve. A slightly smaller proportion of ammonia should then be added to the bulk of the nickel solution. Under these conditions it will be found that practically all the nickel will be precipitated in the form of flocculent nickel hydroxide. If a more concentrated nickel solution be employed or if precipitation be brought about at a lower temperature or if an excess of ammonia be added, the amount of nickel thrown down will be relatively decreased.

After the nickel hydroxide is precipitated it may be applied to a support while still in the solution in which it was formed, or the supernatant liquid may be decanted off. By the use of a very dilute solution of the nickel salt from which the precipitate is formed, practically all of the impurities are said to be removed, when the supernatant liquid is decanted off, whether before or after the application of the precipitate to the support, thus eliminating the necessity of washing the catalyzer. The precipitate and the support are then dried to expel water and are heated to a temperature of about 500° C. in a current of hydrogen.

In accordance with a method of the **Badische Co.\*** a complex, insoluble compound containing one or more easily replaceable bases, e.g., an artificial silicate such as sodium aluminat-silicate ("Permutit"), is treated with a salt of a catalytic metal such as palladium, nickel, copper, zinc, or vanadium, and the salt reduced with hydrogen. The catalytic agents thus produced may be used for the hardening of oils, the hydrogenation or dehydrogenation of organic compounds, etc.†

For treating carbon compounds with hydrogen in the presence of catalyzers the **Badische Co.‡** employ a contact mass composed of a catalytic base metal in intimate contact with silica, shaped as desired.

Carborundum, clay, carbon, alumina, kaolin, amorphous silica, and other substances in a finely-divided condition, are capable of adsorbing colloidal metals, forming bodies which may be used as catalysts, medicinal powders, etc. The substance which is to serve as adsorbent may be brought into a state of suspension in water or other suitable liquid, a solution of a metallic salt added, and the metal precipitated by reduction.§

\* J. S. C. I., 1915, 822.

† See also British Patent No. 1,358, January 27, 1915; U. S. Patent No. 1,256,032, February 12, 1918; Chem. Abs., 1918, 1006.

‡ Swiss Patent No. 72,689, June 16, 1916; Chem. Abs., 1916, 2625.

§ Ges. f. Elektro-osmose G. m. b. H. German Patent No. 252,372, January 9, 1912; J. S. C. I., 1912, 1201.

A nickel adsorption suitable for use as a catalyst is prepared by subjecting an aqueous suspension of silicic acid to the action of an electric arc between nickel electrodes.\*

Richardson † prepares a finely-divided catalytic metal by electrical disintegration, as follows:

Two pieces of a suitable metal are submerged in ether or other fat solvent and an electric current is sent through the pieces which serve as electrodes, these being spaced apart and provided with sufficient current to produce an electric arc across the gap between them, and to cause part of the metal of the electrodes to disintegrate and become diffused in finely-divided form or in colloidal solution or suspension in the fat solvent, forming an organosol. The electrodes may be nickel, copper, platinum, palladium, iron, or their alloys. They may be conveniently used in the form of rods and the electric current may be operated by a hand feed or automatic arc lamp mechanism in which the rods are clamped. The electric current (preferably direct) is operated at a voltage of from 40 to 150. The arc is allowed to continue until the desired amount of disintegrated or finely-divided metal has been produced in the fat solvent. The metal and fat solvent are then separated, as may be done by settling, filtering, or heating until the fat solvent has evaporated. The remaining disintegrated metal is a highly active catalyst, well adapted for hydrogenating oils. This preparation is then mixed with the mass of oil to be hydrogenated, in the proportion of about 1 to 3 per cent of the metal to the mixture, by weight. The mixing is done while hydrogen gas or gas containing hydrogen is introduced into the mixture, and the hydrogenating treatment is preferably done under heat and pressure.

When operating under about 40 lb. pressure and with a temperature of about 160° C., the process of hardening or solidifying of the oil or fat may be completed in from one to eight hours, depending upon the percentage of the finely-divided metal used, the kind of fat or oil being hardened, the rapidity of agitation, etc., and upon the degree of hardness desired.‡

Ellis § comminutes nickel electrically by forming an arc between nickel electrodes under water and levigates to separate light from heavy nickel particles. The sludge of light material is collected and heated with oil to expel moisture.

Elworthy || prepares nickel adherent to the surface of fire brick, pumice or asbestos fiber and the product agglutinated, to form catalytic material.

Aluminum, glass and ceramic surfaces are coated with nickel and other metals by immersing the articles in the heated metal salt solution which contains ammonia and alkali phosphites or hypophosphites.¶

\* British Patent No. 15,287, June 25, 1914, J. S. C. I., 1915, 803 and 1913, 842.

† U. S. Patent No. 1,151,045, August 24, 1915.

‡ See also U. S. Patent No. 1,175,905, March 14, 1916; No. 1,177,896, April 4, 1916; No. 1,257,396, No. 1,257,397, No. 1,257,531, February 20, 1918.

§ U. S. Patent No. 1,092,206, April 7, 1914.

|| U. S. Patent No. 943,627, December 14, 1909.

¶ L'Aluminium Français; French Patent No. 464,721, January 20, 1913; Chem. Abs., 1915, 1376.

The **Oelverwertung G. m. b. H.** describe a process of manufacturing catalytic bodies, for use in effecting reactions in liquids and gases, consisting in heating (thermolyzing) a compound of a metallic nitrate and a soluble organic compound such as sugar. (See page 199.) The resulting voluminous product is reduced by hydrogen at 200° to 300°, a finely-divided and highly active metal powder being obtained.\*

The **Badische Co.**† propose the treatment of fatty acids and esters with nickel, cobalt or iron catalyzer under a hydrogen pressure of at least thirty and preferably of fifty atmospheres while operating continuously.

A catalyzer for oil hardening recommended by the author ‡ is prepared by electrolyzing a nickel solution to form nickel in a highly extended condition, so that a relatively large surface is exposed enabling a small amount of catalyzer to serve in hardening a large amount of oil. The nickel may be deposited independently or on a carbonaceous body such as finely-divided graphite or charcoal.

A form of nickel catalyzer was prepared in the author's laboratory by decomposing silicon tetrafluoride with water which yielded a very voluminous form of silica.

This material was carefully washed free from chlorides and sulphates and dried. An amount of nickel nitrate crystals equal in weight to the silica was dissolved in five parts of water and the solution was thoroughly mixed with the silica. The mixture was dried and ignited until all fumes of nitrogen oxides were expelled. The dark powdery material was heated in a current of hydrogen for one hour at 327° C., cooled and preserved under oil to prevent oxidation. This material carried approximately one-sixth of its weight of nickel. To a quantity of cottonseed oil, an amount of this catalyzer was added to introduce 0.7 per cent of nickel and hydrogen was passed through the oil and catalyzer for 2½ hours at 175° C. At the end of this time the hardened fat produced was found to have an iodine number of 29.8.

**Sabatier** and **Espil**§ have found nickel reduced from the oxide at temperatures above 350° C. is capable of hydrogenating the benzol ring. Frequent assertions have previously been made to the contrary. Sabatier and Espil find that nickel reduced at 500° and maintained for eight hours at 500° to 700° in an atmosphere of hydrogen is still active in this respect. When heated to 750° it would no

\* Italian Patent No. 130,394; March 13, 1913. See also Austrian Patent 70,930, Jan. 10, 1916; Chem. Abs., 1916, 1279.

† German Patent Application No. 73,304, Seifen. Ztg., 1915, 349.

‡ U. S. Patent No. 1,151,003, August 24, 1915.

§ Bull. Soc. Chim., Vol. XV., 1914, 779.

longer act to carry hydrogen to the benzol ring although it was still capable of effecting the reduction of nitro bodies.

**Bacon and Nicolet\*** prepare a catalyzer by impregnating an inert, porous supporting material or carrier, preferably pulverulent, such as kieselguhr, or powdered pumice, with a precipitant for a nickel salt.

Such precipitant may be any suitable hydroxide or carbonate, such as sodium hydroxide associated with a small quantity of a substance which will give a bulky precipitate simultaneously with the precipitation of the nickel salt. This supplemental substance may be, for example, sodium aluminate, and the bulky precipitate therefrom will in such case be aluminum hydroxide. To the support or carrier thus impregnated with the precipitant for nickel and the supplemental precipitant, is added a solution of an appropriate soluble nickel salt, as, for instance, the nitrate. Thereupon, the nickel salt is precipitated as nickel hydroxide by the sodium hydroxide or its equivalent upon and within the catalyst. At the same time, there is simultaneously precipitated the supplemental bulky material by the decomposition of the sodium aluminate. This supplemental bulky material (in this case, aluminum hydroxide) further increases the surface of exposure of the catalyst. The impregnated support or carrier is then washed to remove any injurious soluble products that may be present, and is thereafter dried and the insoluble nickel salt reduced to catalytically active nickel, at a temperature which preferably should not exceed a range of from 350° C. to 450° C. and with a duration of treatment of from one to two hours. If the solution of the nickel salt is absorbed by the support, and the product so obtained made to react with the solution of aluminate and other precipitant, less effective results are obtained.

As an example of the manner of carrying out the process, 100 lb. of the desired carrier, say pumice stone in small fragments, is impregnated with a solution containing 65 lb. sodium hydroxide and sodium aluminate equivalent to 5 lb. aluminum oxide; the precipitating solution containing 165 lb. crystallized nickel nitrate. The product is filtered, washed to remove soluble salts, or most of them, and reduced for two hours, between 350° C. and 450° C. The catalyst made as described should contain about 25 per cent nickel, and about 5 per cent aluminum oxide.

Fragments of glass coated with about 1 per cent of their weight of reduced nickel are recommended by Wells † as catalytic material. The hydrogenation of the unsaturated components of light petroleum oils has been carried out by passage of the oil vapors through a column of contact material composed of nickel-coated glass fragments about 0.5 in. in diameter.

**Sulzberger ‡** finds the reducing power of hydrazine on metal compounds is increased in the presence of a metal of the platinum group, which may be added in the form of a sol. A nickel compound thus

\* U. S. Patent, No. 1,152,591, September 7, 1915.

† U. S. Patent No. 1,179,484, April 18, 1916; J. S. C. I., 1916, 623.

‡ Canadian Patent No. 181,447, Jan 1, 1918; Chem. Abs., 1918, 805.

treated produces a black non-pyrophoric powder which contains nickel, and the metal of the platinum group is an intimate mixture.

Various methods of utilizing nickel carbonyl as a catalyzer in oil hardening are described by the author.\*

The nickel compound is brought into contact with heated oil with or without pressure to decompose the carbonyl and liberate finely-divided nickel. A mixture of nickel carbonyl and hydrogen may be passed into the oil to be hydrogenated liberating nickel in a nascent condition in the presence of hydrogen. Satisfactory results have been secured in the author's laboratory by passing nickel carbonyl vapors into cottonseed oil at a temperature of about 200° C. until a sufficient amount of nickel had been formed to exert the desired rate of catalytic action. The oil is then cooled to about 180° C., and hydrogen introduced. Hydrogenation readily takes place under these conditions even with only  $\frac{1}{10}$  or  $\frac{1}{15}$  of a per cent of nickel present.

#### NICKEL SILICATE

Byrom † prepares a catalyst by precipitating a nickel salt from solution by means of an alkali silicate.

For example, he takes 10 lb. of nickel sulphate, pure and free from arsenic, and dissolves this salt in boiling water to form a saturated solution. Twenty pounds of a solution of sodium silicate (alkaline glass‡) of 100° Twaddle are added and reduced to 25° Twaddle with boiling water; the solution being stirred until the whole of the sodium silicate solution has been added. The precipitate thus formed is transferred to a filter and is washed with boiling water until the filtrate is free from sodium sulphate. The precipitate is pressed to free from excess of water. The operation of filtering may be carried out by the use of a filter press and the combined nickel hydroxide and silicic acid is thus obtained in the form of cakes which, when dry, is porous and can then be ground to a fine powder. The product may be used direct as a catalyst, or it may be reduced to the metallic state by heating in a current of hydrogen at as low a temperature as possible until no water vapor is given off. A temperature of 300° C. is stated to be sufficient for complete reduction. Produced as described the catalyst will contain about 21 per cent of metallic nickel, and in use for the treatment of oils, and fats from  $\frac{1}{2}$  to 1 per cent of catalyst will be required calculated on the percentage of nickel it contains.

Byrom observes that the preparation of catalysts by impregnating inert substances such as kieselguhr, with a solution of a metallic salt, and precipitating the hydroxide or carbonate on the inert substance by adding the required amount of a solution of the alkali hydrates, or carbonates, give products which are difficult to filter and purify. In the case of impregnating kieselguhr with a solution of nickel sulphate and forming nickel hydroxide by adding a solution of sodium hydrate, the precipitate formed is stated to be extremely difficult to

\* U. S. Patent No. 1,138,201, May 4, 1915 and 1,154,495, September 21, 1915.

† British Patent No. 13,382, 1913.

‡ Sodium silicate is manufactured in two qualities known as alkaline glass and neutral glass.



purify and filter so as to obtain the product free from sodium sulphate formed in the mother liquid.

By Byrom's method, it is possible to increase the size of the grains in the precipitate, by allowing the deposited material to stand for a few hours in the solution at a temperature of 80° C. or thereabouts, as the dissolved inorganic salt (sodium sulphate) precipitates the gelatinous matter in the form of flakes, and for the time being prevents the formation of a colloidal solution, and, consequently allows rapid filtration until the precipitate is free from sulphate and impurities. As soon as the precipitate is free from the dissolved inorganic salt it commences to be difficult to filter, as a colloidal or pseudo solution is formed, which passes through the filter, and this is taken as an indication that the precipitate is free from sulphates and impurities. Byrom has found that the catalyst prepared as above described after drying may be used with advantage in the hydrogenation of oils without being reduced to the metallic state. He notes that the metallic hydroxide and silicic acid on being heated to a temperature over 110° C. lose the property of forming colloidal solutions, being transformed into the crystalloids, the grains of which are much larger, and that nickel thus obtained in combination with the silica acts as a catalyst, and the hydrogenation proceeds with greater velocity, than with the fully-reduced catalyst.

Byrom also proposes to use a solution containing 9 lb. of nickel sulphate and 1 lb. of titanous sulphate and thus to produce a mixture of oxides along with the silica.

The silica in combination with the metallic oxide or metal exerts a decolorizing action on the oils treated, and facilitates the separation of the catalyst from the treated product.

Byrom does not indicate to what extent nickel is present as the silicate or what proportion of free oxide or metal exists in the finished material.

Instead of supporting a catalytic metal on a carrier of kieselguhr, kaolin or asbestos Sulzberger\* states he has found that a much simpler method of finely dividing and spreading a catalytically efficient substance over an inert material containing silicon, silica or other compounds containing silicon as follows:

An aqueous solution of a nickel salt is treated with a solution of sodium silicate, the precipitate filtered off, dried and subjected to a current of hydrogen, while being heated. A black powder is obtained. This substance is used as a catalyzer, in hydrogenating oils, with which it can readily be mixed, remaining well in suspension. It is stated that the latter effect may be due to silicic acid in a colloidal condition.†

Sulzberger also recommends ‡ borates, titanates, chromates, and uranates, of metals such as nickel, palladium or platinum. In

\* U. S. Patent No. 1,143,332, June 15, 1915 and Reissue Patent No. 14,167, July 18, 1918.

† J. S. C. I., 1915, 822.

‡ British Patent No. 8,130, June 1, 1916; Canadian Patent, No. 181,287, December 25, 1917; Chem. Abs., 1918, 605.

most cases the catalysts are formed by reduction. E.g., a solution of nickel chloride is treated with sodium silicate to precipitate nickel silicate, which is reduced in hydrogen at a low temperature to give a nickel catalyst. If a small amount of a palladium salt is added to the solution of nickel chloride, the resulting catalyst is rendered more active. These catalysts may be used in the hydrogenation of cottonseed oil.

The regeneration of a spent nickel silicate catalyzer of the type described above is carried out by Sulzberger\* as follows:

The catalyst is largely separated from the oil or other substance which has been hydrogenated and the residue of the latter is removed by extraction or calcination. The catalyzer is then treated with the minimum requisite proportion of caustic soda to dissolve the silica (or boric acid, if nickel borate has been used) yielding the alkali salt. This solution is separated from the residual matter containing nickel and the latter is dissolved in an acid, nitric acid being recommended for the purpose. The acid and alkali solutions are mixed and nickel silicate is again formed. The precipitate is washed to free from soluble salts and is then reduced in an atmosphere of hydrogen gas. Other metal compounds including those of copper, titanium and uranium silicate or borate are stated to be capable of regeneration in a similar manner.

The use of non-abrasive silica in conjunction with nickel and with or without palladium is proposed by Ellis.† The silica may be prepared by passing silicon tetrafluoride into water, collecting and drying the precipitated silicious material and incorporating with a nickel salt or palladium compound.

#### NICKEL BORATE

Schoenfeld‡ observes that oil hardening with the organic salts of nickel such as nickel formate and acetate is a special case of hydrogenation by means of metallic nickel, as these organic salts at the high temperature employed and under the influence of hydrogen are reduced to the metallic state when catalytic action becomes manifest. Schoenfeld has investigated the catalytic properties of an inorganic salt of nickel, namely, nickel borate, and advises that this compound is active as hydrogen carrier for oils and that it does not become reduced during the hydrogenation treatment.

The nickel borate which Schoenfeld used was obtained from Kahlbaum. The salt was of a greenish color, insoluble in water, but soluble in acetic acid and dilute mineral acids. On heating strongly the color changed to a greenish-yellow. In order to improve the catalytic activity Schoenfeld found it advantageous to heat the borate at 300° C. in an atmosphere of hydrogen. By this

\* U. S. Patent No. 1,199,032, September 19, 1916.

† U. S. Patent No. 1,266,782, May 21, 1918.

‡ Siefen. Ztg., 1914, 945.

treatment a large part of the water of crystallization was lost but otherwise apparently no chemical change took place in the borate. Schoenfeld notes that the removal of the water is of importance in connection with the oil hardening for if the water-containing salt is applied directly, a greater part of the water is lost during hydrogenation and because of this change the catalyzer forms lumps which do not distribute well through the oil. Furthermore a higher temperature is required when water-containing borate is directly employed as a catalyzer. To remove the water Schoenfeld heated the borate in hydrogen for one-half hour at 300° C. in an electrically-heated glass tube. The product so obtained was of a dark grey color. After such heating analysis showed the following composition:

NiO.....	44.73%
B <sub>2</sub> O <sub>3</sub> .....	42.01%

Calculated for NiB<sub>2</sub>O<sub>4</sub>·H<sub>2</sub>O.

NiO .....	45.9%
B <sub>2</sub> O <sub>3</sub> .....	43.0%

These results, therefore, indicate the compound to be nickel metaborate containing 1 molecule of water of crystallization. The remaining water of crystallization may be removed by protracted heating at 300°. For technical application it is not necessary, however, to remove all the water, as the activity of the catalyzer is not increased by such protracted heat treatment.

The catalytic activity of the compound was determined in the following simple manner:

One hundred to 200 g. of the oil with 1 per cent of the nickel borate were placed in a flask of about  $\frac{1}{2}$  liter capacity and were heated to 160° to 180° C. while hydrogen was passed through the oil. After the hydrogen was introduced in this manner for a short time the contents of the flask acquired a greyish color as the result of the fine distribution of the catalyzer in the oil. Hydrogen was applied for 2½ to three hours and the oil then filtered through paper. The residue of the catalyzer was extracted with ether and benzene until supposedly free from oil, but on treatment with dilute mineral acids, oily drops separated. It was, therefore, concluded that during the hardening some of the free fatty acid present in the oil combined with nickel, forming a metallic soap with liberation of boric acid. To ascertain if this were the case 5 g. of the used catalyzer were dissolved in dilute hydrochloric acid and the oil which separated was extracted with ether and purified. The oil obtained was yellowish in color and contained about 50 per cent of free fatty acid corresponding to an acid number of 98. The acid number of the original oil was 0.3. After the hardening operation the nickel borate was found to contain less boric acid than corresponded to the original formula.

#### ANALYSIS OF NICKEL BORATE USED FOR HARDENING

	NiO	B <sub>2</sub> O <sub>3</sub>
1. Used once.....	42.07	28.3
2. Used twice.....	44.3	33.84
3. (a) Used once.....	43.5	34.9
(b). Used twice.....	43.88	33.5
(c) Used three times.....	45.5	29.42

In investigation (3) an endeavor was made, by careful drying of the hydrogen to reduce the formation of fatty acid to a minimum. The same mass of cata-

lyzer was used four to six times for hardening without any diminution of its activity. From the following observations Schoenfeld concluded that catalysis was due to nickel borate alone and not to the small amount of nickel soap present for the reason that (1) the temperature of 160° to 180° was regarded as insufficient to cause nickel soap to become active; (2) the amount of the latter was too slight to effect any considerable change, and (3) if the nickel soap were responsible for hydrogen addition the activity of the nickel borate catalyzer would increase with repeated use as a result of the increase in the amount of nickel soap. Schoenfeld found that as the content of nickel borate is reduced the activity of the catalyzer correspondingly diminishes. Various oils were treated with the borate catalyzer, including cottonseed, rape, linseed, soya bean and whale oil, and satisfactorily hardened products obtained. In one experiment made by Schoenfeld 200 g. of cottonseed oil were mixed with 2 g. of nickel borate and heated for three hours at 160 to 170° in a stream of hydrogen. The solidifying point of the hardened oil was 38° C. By longer action of the hydrogen a solidifying point of 47° was obtained. The application of pressures of one-half to one atmosphere somewhat improved the reaction so that in two hours linseed oil, for example, was converted into a fat of the consistency of tallow with a solidifying-point of 38°. The hardened oils which Schoenfeld prepared by means of nickel borate possessed a pure white color and the acid number was not increased by the hardening treatment. Schoenfeld regards nickel borate especially desirable as a catalyzer because it appears that the ordinary catalyzer poisons such as sulphur do not effect the activity of the borate. Schoenfeld in fact added sulphur to cottonseed oil and claims no detrimental effect was incurred thereby. He summarizes the advantages of using nickel borate, as follows: The hardening occurs at a relatively low temperature (160° to 180° and in most cases between 160° to 170°). The application of gas under pressure is not necessary, and the hydrogenation can be carried out in very simple apparatus. The lack of sensitiveness to catalyzer poisons and the ability to use the nickel borate repeatedly also are advantages.

Erdmann and Rack\* carried out various tests with nickel borate which lead them to regard Schoenfeld's conclusions as unreliable.

It was noted that Schoenfeld used Kahlbaum's nickel borate containing slightly more nickel than corresponded to the formula  $\text{NiO} \cdot \text{B}_2\text{O}_3$  on linseed oil and also on the easiest of all fatty oils to harden, i.e., refined cotton oil.

No hydrogenating action was observed with either hydrated or anhydrous nickel borate at a temperature of 175° C. Green nickel borate was heated for one-half hour at 330° to 340° C., in a stream of nitrogen. Four grams of this borate material was introduced into 400 g. of cotton oil which previously had been heated to 100° C. The temperature was raised to 175° C. and a stream of hydrogen at the rate of 20 liters per minute was passed through the oil for three hours. No hardening occurred. Linseed oil gave the same results.

Green nickel borate was heated in hydrogen at 300° to 305° C. for one-half hour, and during this treatment the color of the material changed from yellowish brown to grey. An aqueous solution of phosphomolybdic acid was colored blue on standing with some of the grey product. Cotton oil treated for 9½ hours

\* Seifen. Ztg., 1915, 3.

with this hydrogen treated material hydrogenated only slightly indicating very weak hydrogenating power.

A quantity of the borate was exposed to hydrogen at a temperature of  $340^{\circ}$  and a dark grey product obtained. Under the same conditions except in an atmosphere of nitrogen a yellowish brown material resulted. While the latter material was neither magnetic nor reactive with phosphomolybdic acid, the dark grey product was attracted by a magnet and colored phosphomolybdic acid strongly blue. Some of the grey product was pressed to form a block and a current of electricity at 80 volts used to test its electrical conductivity. No passage of the current could be detected when employing a sensitive milliamperemeter, from which Erdmann concluded that no metallic nickel, but nickel suboxide, was present. On treatment with dilute mineral acid hydrogen was evolved in an amount corresponding to 7.4 per cent nickel suboxide ( $\text{Ni}_2\text{O}$ ).

Four grams of the dark grey product were mixed with 400 g. of edible cotton oil and on heating to  $175^{\circ}$  to  $180^{\circ}$  C., a hydrogen stream (20 liters per minute) was passed through the oil for three hours when the solidifying point of the latter was found to be  $31.8^{\circ}$  C. The catalyzer distributed well through the oil in the manner characteristic of nickel suboxide and due, it is stated, to the formation of an organosol. The recovered catalytic agent did not exhibit any electrical conductivity.

Five hundred grams of cotton oil were heated to  $125^{\circ}$  C., 15 g. green nickel borate were added and the temperature was then raised to  $260^{\circ}$ . A stream of hydrogen was passed through the oil for five hours, and the oil was found to be hydrogenated to a solidifying point of  $31.8^{\circ}$ .

As is known, boric acid is a very weak acid body and the salts of mono- and tri-basic boric acid are, therefore, very unstable. Salts of the nature of borax derived from tetra boric acid are more stable. On heating nickel borate  $\text{NiO} \cdot \text{B}_2\text{O}_3$  to  $300^{\circ}$  it is likely that nickel oxide and tetra borate form according to the equation  $2\text{NiB}_2\text{O}_4 = \text{NiB}_4\text{O}_7 + \text{NiO}$ .

By treatment with hydrogen for one-half hour at  $300^{\circ}$  or even at  $340^{\circ}$  C., nickel suboxide, not metallic nickel is stated to be formed. While pure nickel oxide is readily reduced to the metallic state by hydrogen at  $300^{\circ}$  C., this is held not to occur in the presence of boric acid, which acts to retard reduction. This acid belongs to a class of bodies which so hold back the reducing reaction that either resort must be had to higher temperatures to secure the metal, or the intermediate suboxide phase obtains according to circumstances.

**Summary.** 1. Neither hydrated nor anhydrous nickel borate has proven active as a fat-hardening catalyst at a temperature of  $175^{\circ}$  C.

2. By heating nickel borate in hydrogen at  $300^{\circ}$  to  $340^{\circ}$  C., a partial reduction to the suboxide of the nickel oxide present in the borate, occurs. Due to the presence of the suboxide, the material subdivides in fatty oils and acts catalytically at  $175^{\circ}$  although less effectively than pure nickel suboxide.

3. If a fatty oil is heated with green nickel borate to  $260^{\circ}$  C., and treated with hydrogen, decomposition occurs with formation of nickel oxide and suboxide and these products act as hydrogen carriers in the same manner as the decomposition products of organic nickel salts such as nickel acetate have been observed to function.\* It is claimed by Erdmann and Rack that Schoenfeld is in error in ascribing the hydrogenation of fats when using nickel formate, acetate,

\*Journ. prakt Chem. (N. F.), 87, 449, and 452.

etc., to the agency of metallic nickel, as nickel oxides are considered responsible for the reaction.

4. No advantages over nickel oxide have been found in nickel borate. The low temperature of hardening observed with the latter is merely a consequence of the prior formation of nickel suboxide. The property of the latter to act as a hydrogen carrier at a temperature below 200° C., was already known. The advantages ascribed to nickel borate by Schoenfeld, namely, that no hydrogen pressure above atmospheric is required hence the hydrogenation process may be carried out in very simple apparatus, the slight degree of sensibility to catalyzer poisons, the ease of separation of the hardened product from the catalyzer, the ability to use the catalyzer repeatedly, are all features of value applicable to the nickel oxide process as pointed out in German Patent No. 266,438 and elsewhere. Nickel borate possesses the practical disadvantage that it affords nickel oxide loaded with material of no value in the hardening process.

**Nickel Borate.** Normann\* refers to hydrogenation by means of organic nickel salts such as the formate, acetate, stearate and oleate as only a special case of usage of metallic nickel as a catalyzer as formation of the metal always occurs before hardening takes place.† In fact the liberation of organic acids in a state of purity is secured in many cases by passing hydrogen into the corresponding salt of nickel ‡ affording a technical process for the preparation of pure concentrated organic acids. It also is known that inorganic salts of nickel can be reduced by hydrogen to the metallic state § and that catalyzers have been prepared by the reduction of inorganic nickel salts.||

It is to be expected that nickel borate would be broken down to a greater or less degree into metallic nickel and free boric acid on heating in a stream of hydrogen. This decomposition actually occurs, but when reduction takes place below 300° but very little boron trioxide volatilizes.

On heating nickel borate in an electric furnace at 300° in a current of air, some boric acid sublimes and the borate turns to a deeper shade of green. Water hydrolyzes the borate, forming free boric acid and nickel hydroxide.

Nickel borate was heated in a current of hydrogen for one-half to three-quarters of an hour at temperatures ranging from 300° to 400° C. The product reduced at 300° was used to hydrogenate cottonseed oil and in three hours treatment at 170° to 180° C. the iodine number was reduced from 108 to 104.5.

By reduction of the borate at 350° an iodine number of 101.4 was obtained under otherwise similar conditions. The borate reduced at 400° was considerably darker in color, and cotton oil treated with it exhibited an iodine number of 47.7. No hydrogenation of the oil was perceptible when using nickel borate without previous reduction.

In order to show the presence of free metallic nickel in this borate catalyzer the carbon monoxide method ¶ was applied. It was found that free boric acid prevented the reaction between carbon monoxide and nickel. Accordingly the reduced and cooled borate was introduced into water (in an atmosphere of carbon dioxide to prevent contact with oxygen), the mixture warmed on the water-

\* Seifen. Ztg., 1915, 46-47.

† Meigen and Bartels, Journ. prakt. Chem., 1914, 89, 290.

‡ German Patent No. 217,846.

§ Gmelin-Kraut V, 1, 23, 1909.

¶ Journ. of Gas Light, 1, 7, 13, page 31.

¶ Chem. Ztg., 1915, No. 6 and No. 7/8.

bath and filtered in such a manner as to avoid contact with air. The precipitate, thus freed of boric acid, was dried in hydrogen below 100° C., and after drying was exposed to carbon monoxide. The gaseous products of reaction were passed through a heated tube of glass and the rate of formation of a nickel mirror noted. The borate reduced at 300° and 350° quickly yielded a slight but distinct nickel mirror while the product reduced at 400° formed a heavy mirror. This is considered proof of the presence of metallic nickel in the reduced borate and the former only is responsible for hydrogenation.\*

**Erdman** and **Rack** † believe the fact is fully established that nickel sub-oxide is formed when nickel borate is heated in oil at 260° C., and hydrogen passed through the vehicle, also that the same product is obtained by reducing the borate as a dry powder at 340° C., with hydrogen gas.

Erdmann states he does not know whether or not metallic nickel is formed at 400° C., as he has made no observations at so high a temperature, but that it is probable the increase in temperature has, in this case, the same influence on the progress of reduction as has been noted with organic salts of nickel. Bedford and Erdmann ‡ found nickel oxide to be formed when such organic salts were heated in oil through which a stream of hydrogen was passed, and only under special conditions such as a substantial increase in the temperature was metallic nickel produced. Erdmann also observes that Normann refers to Meigen and Bartels as confirming the view that hydrogenation with organic nickel salts is only a special case of operation with metallic nickel, although Meigen and Bartels are stated not to have published anything touching on this point. Erdmann reiterates that this view is wholly erroneous. He questions the credibility of Meigen and Bartels' results in other respects.

Also it is asserted by Erdmann that he was aware phosphomolybdic acid was not a reagent suitable to distinguish nickel from its suboxide as both bodies react to form molybdenum blue, but that this reagent was employed on the nickel borate to show that reduction had taken place. On the other hand, Erdmann regards as positive proof of formation of nickel suboxides: (1) the black color resulting from subdivision of the catalyzer during its formation in oil and (2) the lack of electrical conductivity of the used and fat-free catalytic agent. The conductivity also increases with increase in temperature.§

**Schoenfeld** || discusses the observations of **Bosshard** and **Fischli** ¶ who, Schoenfeld notes, on the basis of an experiment with oleic acid, have stated that in the hydrogenation of oils in presence of nickel borate, catalytic action comes into play only after the borate is decomposed.

\* See also Normann and Schick, *Arch. Pharm.*, **252**, 208-210, 1914.

† *Seifen. Ztg.*, 1915, 75.

‡ *Journ. prakt. Chem.* (2) **87**, 449.

§ *Seifen Ztg.* 1915, 288.

|| *Z. angew. Chem.* 1916, **29**, 39; *J. S. C. I.*, 1916, 367; *J. Chem. Soc.* **110**, 1, 248.

¶ *J. S. C. I.*, 1915, 1079.

Schoenfeld points out that his conclusions in regard to the favorable action of nickel borate as catalyst referred only to neutral fats and that he was aware of the decomposition of nickel borate by free fatty acids. In Bosshard and Fischli's experiment, the activity diminished with increasing decomposition of the catalyst, and this confirms Schoenfeld's contention that nickel borate is a more effective hydrogen carrier than the mixture of nickel and nickel oxide (with boric acid) formed by its decomposition. In many cases hardened fats (especially from marine animal oils) produced with the aid of nickel or nickel oxide contain more nickel than those prepared with the aid of nickel borate. Schoenfeld disputes the statement of Bosshard and Fischli that the catalytic hydrogenation of oils in presence of nickel borate is conditioned by the previous decomposition of the salt; the reverse, in fact, he claims is the case, for with increasing decomposition of the borate owing to the action of the free oleic acid used in Bosshard's experiment, the activity of the catalyst diminishes. The relatively high nickel content of the oleic acid hardened in presence of nickel borate is likewise to be attributed by Schoenfeld to the decomposition of the salt by the free fatty acid.

C. and G. Muller Speisefettfabrik A.-G.\* employ a hydrogenation catalyzer consisting of a nickel salt of an inorganic acid not volatile at the temperature of hydrogenation (e.g., nickel borate or silicate). The nickel salts are preferably heated in a current of hydrogen before use.

The action of nickel borate as a catalyzer has been determined in the author's laboratory. A nickel compound was prepared by treating a solution of nickel sulphate with sodium metaborate. The voluminous precipitate which formed was dried in the air at 100. C. and subsequently dehydrated at a higher temperature in a current of hydrogen. This product hardened cottonseed oil at about the same rate as the catalytic material used by Schoenfeld.

A catalyzer described by Bremen Besigheimer Oelfabriken † is produced by calcining organic metal compounds, or a mixture of metal compounds with carbon or carbon-containing substances, and introducing the mixture, immediately after calcining, into oil or other indifferent liquid in which it can be kept indefinitely.

It is essential that the calcining should be continued until the mixture has become pyrophorous; as this quality is stated to greatly increase the catalytic action of the material.

The observation is made that it has been previously proposed to heat or burn organic metal compounds or mixtures of metal compounds and carbon to produce finely-divided catalytic materials, but that it has never been proposed to introduce the materials so produced directly into oil, immediately the desired stage of the calcining has been reached; also that catalysts produced by reduc-

\* French Patent No. 470,364, March 28, 1914; J. S. C. I., 1915, 186; Swedish Patent No. 41,331, September 13, 1916; Chem. Abs., 1916, 3172.

† British Patent No. 4023, 1915.



tion in a current of hydrogen have previously been rubbed up with oil to form a viscid "emulsion-like fluid," and the suggestion has been advanced to mix a metal compound with oil or other protective substance and reduce the mixture in the presence of hydrogen. In the present case, however, it is noted that the expensive, lengthy and dangerous reduction with hydrogen is entirely avoided.

Fats hydrogenated with the ordinary catalyzer, are stated to have a peculiar smell which is designated as "catalyzer smell." To eliminate this smell, the fats have to be steamed after hydrogenation. This steaming usually is regarded as unnecessary when catalyzers prepared by calcination are used. The carbon is claimed to remove the typical catalyzer smell, so that when hydrogenating with the aid of these catalyzers, substances are obtained that can be used at once for technical purposes. Owing to the presence of carbon, the fat is found to be more easily filtered and at the same time bleached, as pyrophorous carbon has bleaching properties.

The process may be carried out in the following manner:

Benzoate of nickel is heated above  $1000^{\circ}\text{C}$ . until carbonized, and the carbon has completely or partly reduced the oxide of nickel formed. The so-called mixture of carbon and metal is then at once mixed with oil, or other indifferent liquid. The calcination reaction is found to reach completeness in a few minutes, or at the outside in half an hour.

In a second way of carrying out the process, carbonate or oxide of nickel, precipitated on fossil meal, is mixed with about the same quantity of fine carbon, and heated above  $1000^{\circ}\text{C}$ . until the mass has become pyrophorous. It is then introduced without delay into oil and is thoroughly mixed with the latter. This catalyzer may then be mixed with a further quantity of oil. Its lasting qualities are very good.

Oil hardening with such catalyzers can be carried out at  $150^{\circ}$  to  $200^{\circ}$ . Carbon, which by itself becomes pyrophorous on being calcined, such as, for instance, animal charcoal, is recommended. This is regarded as apparently due to the fact that pyrophorous carbon alone has a catalyzing action, and also assists the metal catalyzer in its catalytic action.

The application of nickel boride\* and of nickel carbide† or of catalyzers containing the latter is proposed by Ellis. The catalyzer may be sealed in paraffin wax.

The preparation of a catalyzer from inorganic basic compounds is described by Ellis.‡

One form of this catalyzer is prepared by subjecting nickel hydrate to the reducing action of hydrogen in a submersion or bathing liquid of oil or glycerine. The reduction is carried out at so low a temperature that the catalytic material is left in a relatively voluminous condition. By the reduction of mixtures of nickel hydrate and other metallic hydrates such as copper hydrate, a composite metal powder is obtained which is particularly active in the hydrogenation of some oils. The composite catalyzer of nickel and copper has been found effective

\* U. S. Patents No. 1,201,226, Oct. 10, 1916; 1,255,590, Feb. 5, 1918; J. S. C. I., 1918, 214 A.

† U. S. Patent No. 1,182,995, May 16, 1916.

‡ U. S. Patent No. 1,156,068, October 12, 1915.

in the hardening of commercial oleic acid. A method of preparing nickel hydrate in a form suitable for reduction to yield catalytic nickel is described by Ellis.\*

Some interesting observations have been made by Kelber† on the catalytic hydrogenation of organic compounds with non-noble metals at room temperature.

The catalytic action of the reduced nickel metals is stated to be greatly increased if the compounds employed (best the basic carbonates) are first deposited on a suitable carrier (infusorial earth, Florida clay, the various commercial hydrosilicates of aluminum and magnesium, blood charcoal, the decolorizing charcoal of the ferrocyanide manufacture, linden charcoal, etc.). The reduction is best effected in aqueous or aqueous-alcoholic solutions. In alcohol, benzol, acetone, ethyl ether and ethyl acetate it is slower; the addition of a little water, especially with ethyl ether and ethyl acetate, greatly accelerates it; in acetic acid it is rapid with nickel reduced at 310°. Chloroform is not suitable. To get an approximate comparison of the catalytic action of reduced non-noble metals with that of colloidal palladium, the detonating gas catalysis was carried out; Kelber and Schwarz palladium preparation ‡ was used; 0.2 g. this (=0.0344 g. Pd) showed an activity which at first was less than that of 0.5 g. nickel (α) (from the basic carbonate) reduced on 4.5 g. of an inorganic carrier in hydrogen at 450°, although it gradually increased as compared with the activity of the nickel and finally surpassed it. A nickel prepared at 310° or 450° without a carrier gave a negative result. In the reduction of 0.75 g. cinnamic acid in 50 per cent alcohol, however, preparation (α) and 3.0 g. nickel reduced at 450° have about the same effect as 0.5 g. reduced at 310°, while 0.5 g. reduced at 450° without a carrier is enormously less effective than preparation (α); in an aqueous alcoholic solution of sodium cinnamate the nickel reduced at 310° has the same effect as an equal weight of nickel reduced at 450° on a carrier. Cobalt may be used instead of nickel but the reduction is slower. Other substances reduced in this way were sodium phenyl propionate, quinine hydrochloride, diphenyldiacetylene, sodium "cotton oleate." Details of the various experiments showing the amounts of hydrogen absorbed in different time intervals are given.

Fuchs§ observes that carbonates of some base metals, such for instance as nickel carbonate, can be converted directly into metals in a very finely-divided condition by immersing or suspending this material in the fatty acid or oil to be reduced and heating in the presence of hydrogen to the specific reduction temperature for each compound, which lies between 210° and 290° C. After the formation of the catalyzer is complete the temperature is lowered and the reduction of the oil is effected. By such procedure the catalyzer is prevented from coming into contact with the air. In plants where

\* U. S. Patent No. 1,165,956, Dec. 28, 1915.

† Chem. Abs., 1916, 837; Ber. 49, 1916, 55-63.

‡ Chem. Abs. 6, 2757.

§ Chem. Abs., 1914, 3636; British Patent No. 11,542, 1913.

hydrogenation is performed with the circulation of a hydrogen atmosphere the employment of organic salts of metals is held by Fuchs to be impracticable because the oxide of carbon which is constantly generated cannot be eliminated from such hydrogen atmosphere except at high cost. As an example of Fuchs' method, castor-oil is mixed with 1.2 per cent of finely-powdered and preferably freshly-prepared nickel carbonate previously dried at a temperature of 110° C. and the mixture is then heated to a temperature of 230° C. while a current of hydrogen is allowed to pass slowly therethrough. As soon as this temperature is attained, compressed hydrogen (twelve to fifteen atmospheres) is admitted into the mixture through a nozzle. The reduction of the salt to metallic nickel takes place with a slight frothing due to the evolution of water. As soon as this operation is completed the temperature is lowered and the reduction of the oil is carried out as an uninterrupted continuation of the preceding operation.

Catalytic substances such as metals on an inert carrier which have been used in hydrogenating oils or fats are regenerated according to **Morrison's** method\* by expressing most of the oleaginous material from the catalyst so as to form the latter into briquets or cakes, burning out residual organic substances and then recovering the metal in catalytically active form by heating in hydrogen.

Morrison observes that great difficulty is experienced in revivifying metallic catalysts, either wholly metallic or on an inert support, which have been "spent" in the hydrogenation of fats and oils. The most direct way is to dissolve out the fats, etc., with a suitable solvent, then reduce in an atmosphere of hydrogen. It has been found that there is much organic matter present, which is not soluble in ordinary solvents and when it has been sought to burn out this organic matter difficulties arise. If a reducing temperature or temperature below the point of ignition in the air is employed, the material is apt to char, leaving a great deal of carbon in the material. If the material is heated in an oxidizing atmosphere and at a temperature which will burn out all the organic matter, it is found that it is not catalytically active when reduced in hydrogen. Further it is very difficult to burn out completely a light pulverulent material without frequent turning over, to expose the unburned portion to the air. In turning it over, it dusts easily, entailing losses. Morrison recommends that the material as it comes from the filtering or settling apparatus, either after being extracted with a suitable

\*U. S. Patent No. 1,203,233, October 31, 1916; Chem. Abs., 1917, 105.

solvent or direct, containing all the oil and organic matter, be subjected to pressure, preferably in a hydraulic press, at about 2000 lb. per square inch in order to extract as much oil as possible. Cakes or briquets are thus formed, which can be readily and completely burned out, without the necessity of turning them over to better expose to the air, as the lumps allow a free circulation of air. After the material is sufficiently burned (a small per cent of carbon does not interfere), it is macerated with water and sufficient mineral acid is added to dissolve all the metallic portion. This is done in a vessel which contains a mechanical agitator to keep the material in suspension. When the metal or oxide is dissolved and still while agitating the metal salt is precipitated as a hydrate or carbonate by sodium carbonate. It is now washed practically free of any soluble salts which would interfere with its activity, i.e., salts which would act as "poisons" either before or after reducing, such as sodium sulphide or sodium sulphate. A washing filter press is recommended for this purpose. The washed product is dried, ground and reduced in an atmosphere of hydrogen. Morrison states that it will be found to have regained its original activity.

Nickel oxides used as catalytic agents in the hydrogenation of oils may be regenerated by removing the grease, calcining with limited access of air so as to produce suboxide, or with free access of air to produce monoxide, washing if necessary (e.g., if a chlorinated solvent has been used for extracting grease) and drying. The monoxide thus obtained may be converted into suboxide by a limited dry reduction by hydrogen, the operation not being pushed so far as to produce a pyrophoric product.\*

A catalyzer rendered inactive by adhering fat is treated by Haas,† in an autoclave, under pressure to saponify the fat.

In using nickel in a colloidal form difficulty is experienced in the filtration of oil in which such a body is suspended and Ellis‡ has proposed the filtration of oil containing colloidal nickel through a bed or layer of hydrated silicic acid or silicate such as zeolite or natural silicate containing hydrous material.

In carrying out this process the bulk of the catalytic material may be removed by coarse filtration. The oil carrying the finer particles of the catalyzer is passed through a filter containing the hydrated silicic acid or hydrated silicate. An ordinary filter press may be used for this purpose and the silicious material may be applied to the filter cloths by passing through the press a quantity of hardened oil in a molten condition containing the silicious material, thereby

\* *Soc. Industrielle de Produits Chimiques*. British Patent No. 112,768, Nov. 5, 1917; Chem. Abs., 1918, 1258.

† Norwegian Patent No. 28,034, July 2, 1917; Chem. Abs., 12, 98.

‡ U. S. Patent No. 1,224,291, May 1, 1917.

forming a silicious coating on the filter cloths. An effective form of filtering agent is prepared by precipitating silicic acid on kieselguhr or fuller's earth.

**Bosch, Mittasch and Schneider** \* suggest a form of catalytic material useful for carrying out hydrogenation and dehydrogenation rapidly, with certainty and at comparatively low temperatures. An intimate mixture of a common metal, iron, nickel, cobalt and copper, with a phosphate of an alkaline earth metal as a promoter, is employed. It is necessary to effect an intimate mixture of the catalytic metal and the promoter. If calcium phosphate be employed as the promoter, the oxide or carbonate of the catalytic metal can be mixed with calcium phosphate and the mixture thereupon be heated and reduced. A still better method consists in taking an insoluble salt, such as the carbonate, or an oxide of the catalytic metal, and adding to it a solution of a calcium salt, for instance, calcium nitrate, and then to add the necessary quantity of phosphoric acid either as such or in the form of ammonium phosphate, or alkali metal phosphate, in order to convert the calcium into phosphate. It is preferred to employ basic phosphates, such as tricalcium phosphate, as promoters.

It is advantageous for the purpose of making a very active contact mass to prepare the catalytic metal from carbonaceous salts or mixtures of such salts, for instance, from carbonates or from formates. It is often useful to add to the mixture, bodies of inorganic or organic nature, which act either as carriers, or as binding agents, or which increase the porosity of the contact mass. Asbestos, charcoal, or pumice may be used. The catalytic metal can be employed either in a state of fine division, or in a more compact form, such as wire netting, or wool, or in sheet form.

Catalytic mixtures made according to this method can be used for the hydrogenation and dehydrogenation of compounds containing carbon and are of particular value for the hardening of fats and fatty acids.

The reaction can be carried out either at ordinary pressure, or under increased pressure, for instance, above fifty atmospheres and in most cases proceeds sufficiently rapidly at temperatures below 180° C.

*Example:* Suspend 5 parts by weight of nickel carbonate in a solution of 1.3 parts of calcium nitrate, and then precipitate the calcium by the addition of 0.7 part of ammonium phosphate ( $\text{NH}_4\text{H}_2\text{PO}_4$ ). Filter, wash well, dry and reduce with hydrogen at

\* U. S. Patent No. 1,215,335, February 13, 1917. See also No. 1,271,013, July 2, 1918.

about 350° C. This contact mass may be employed in the reduction of cottonseed oil by means of hydrogen at about 130° C. In another case\* the same investigators employ an oxide of boron as a promoter and as an example they recommend to mix freshly-precipitated nickel carbonate with 10 per cent of its weight of ammonium borate previously dissolved in water. The product is dried and reduced. Calcium borate may be similarly used. This catalyzer is recommended for hardening fish oil.

#### ORGANIC SALTS OF NICKEL AS RAW MATERIALS FOR CATALYZERS, METALLIC FORMATES AND OLEATES

Snelling † observes that in the use of a siliceous carrier with an oxide it is difficult to prevent more or less formation of sluggy compounds, but that a catalyzer of high reactivity can be prepared by heating the metallic formates, the reduction of which takes place at a very low temperature, and proceeds smoothly.

Nickel, cobalt, iron and copper formate, etc., may be used; and these salts may be employed in the dry state where a powder is required; or a porous carrier may be soaked with a solution of the formate, dried and reduced. On heating, the formates decompose with an evolution of carbon monoxide and hydrogen, both strongly reducing gases; and this evolution of these gases in statu nascendi, allows the formation of highly reactive metal at very low temperatures. It is not necessary as in the case of nitrates, to supply the reducing means from another source; which is regarded by Snelling as an advantage in the case of forming the catalyst on a support. In the formates, the combustible and the oxygen of the metal oxide are in atomic or molecular contact; a contact differing from that of the oxide as powder in an atmosphere of hydrogen. And, as the reduction of the metal oxide and the oxidation of the combustible as a total reaction is exothermic, a reduction change started in one portion of a mass of formate tends to spread through it; the reaction it is stated can be initiated at one point and allowed to spread through the material as a self-propagating reaction. The reduction may be effected at a comparatively very low temperature; a temperature at which there is no tendency of the reduced metal to sinter or of the oxides to slag.

In making reactive copper where the metal is desired in pulverulent form, copper formate is first dried at a low temperature and is then cautiously heated in a container to the lowest temperature at which the formation of metal becomes evident. The air in the tube is best displaced by hydrogen prior to heating. The formate may be dried in the container in which reduction is subsequently to be effected. In so doing it is advantageous to pass through a stream of hydrogen or other non-oxidizing gas. This stream carries away as fast as formed the water produced in drying and that produced in the subsequent reduction and much facilitates both operations. A vacuum may be used in lieu of hydrogen.

\* U. S. Patent No. 1,215,334, February 13, 1917.

† U. S. Patent No. 1,122,811, December 29, 1914; J. S. C. I., 1915, 182.

Where the copper is carried on a support, the carrier may be soaked in a solution of copper formate and the impregnated material dried and heated in the same way. It is particularly advantageous in this case after placing the impregnated carrier in the reduction vessel to produce a vacuum to remove adsorbed air. Hydrogen is then allowed to enter and the material heated.

The porous carrier employed may be any of the usual refractory materials. For nickel, cobalt, iron, copper, etc., where used for hydrogen addition, as in hardening fats, the carrier may be coke. Where used in oxidizing reactions, as in the manufacture of formaldehyde, the carrier is better an inoxidizable material such as pumice-stone, baked clay, kieselguhr, etc. For many purposes Snelling finds that alundum is a desirable carrier since in some reactions alumina has a catalytic action. It is particularly advantageous in making a copper catalyst for the manufacture of formaldehyde.

For many purposes in catalytic operations Snelling states it is desirable to have a column of catalytic material wherein the carrier has different proportions of catalyst at different points throughout the column. For example, in making formaldehyde from methyl alcohol and air it is advantageous to have the mixed vapor and air pass through an alundum carrier containing a relatively small amount of copper, then past a carrier containing more, and so on until the mixture finally passes a carrier relatively rich in catalyst. It is regarded as advantageous to have the concentration of the reactive bodies inversely proportional in any given zone of catalysis. Similarly in hydrogenation processes involving the addition of hydrogen to vapors and gases, it is advantageous to have the gas mixture first pass through a carrier containing relatively little reduced nickel and subsequently past a carrier containing more nickel.

As stated, the reduction of the formate should be at the lowest possible temperature; and the material should be brought at this temperature rather gradually. Careful observation of any given formate will show to the eye the point where reduction begins. Any violent heating causes a sudden decomposition of the formate with the liberation of carbon monoxide and hydrogen in the gaseous form; after which reduction can only be in the ordinary way; viz., by a reducing atmosphere. With violent heating the reaction, under the catalytic influence of the metal, is apt to be irregular and result in the production of carbon and other bodies.

**Spieler** \* states he has found that gelatinous aluminum hydrate, also gelatinous silicon hydrate possess catalytic properties in a slight degree, not sufficiently marked to be of value as a commercial catalyst when used by themselves; however, when in contact or in combination with nickel salts the catalytic properties of these hydrates are remarkably increased, so much that such a compound or combination has far greater catalytic activities than either of the component ingredients themselves.

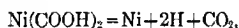
When a nickel salt of an organic acid, such as nickel formate (also nickel carbonate), is intimately incorporated with a preponderating quantity of inorganic colloids, such as gelatinous aluminum hydrate or gelatinous silicon hydrate,

\* U. S. Patent No. 1,139,592, May 18, 1915.

either singly or together, in the dry state, or with water to form a pasty mass, and this heated with a quantity of fat or oil to a temperature approximately 230° to 250° C. in a pressure vessel arranged to agitate the contents, a catalyzer of uniform activity and stability can be produced.

In preparing this catalytic compound, in the event the chemical ingredients are in the form of a pasty mass, during the stage of the evaporation of the water and the subsequent heating to the final temperature, a brisk agitation of the mass is desirable, as by this procedure the entire catalytic substance is finely and uniformly distributed throughout the suspension medium.

During the stage of evaporation of the water of solution, some intermediate reactions may occur between the nickel formate or carbonate and the inorganic colloids; however, the final decomposition of the nickel formate may be expressed by the equation



and that of the nickel carbonate as



The hydrogen liberated during the decomposition of the formate is in the nascent state and within the oil-covered particles is absorbed by the catalyzer, which is then fully charged with the hydrogen content it is capable of occluding. In this manner the catalyzer is preserved in its most potent state.

A convenient method of preparing this catalyzer is to take 40 parts of nickel formate and carbonate in aqueous suspension and thoroughly incorporate this with about 80 parts of gelatinous aluminum hydrate or gelatinous silicon hydrate, either singly or together, in any proportion. The proportion of nickel formate and carbonate may be varied considerably. The proportion may be as low as 4 parts of one to 36 parts of the other with satisfactory results. This mixture is placed in an agitating vessel with 100 parts of a suspensory medium (oil) and the whole mass is heated with constant agitation. The steam resulting from the evaporation of the aqueous solution is allowed to escape. When the water has been driven off, the temperature is raised to approximately 235° to 250° C. and this temperature maintained until the reaction is complete.

Another procedure is to take nickel formate and carbonate, and air-dried gelatinous aluminum hydrate or silicon hydrate, or both together, thoroughly incorporate these and put in a pressure vessel with a quantity of fat or oil, agitate and heat the mass to a temperature of approximately 235° to 250° C. until the reaction is complete.

**Higgins** \* notes that in order to prepare a catalytic body from fatty acid salts of nickel and cobalt it is not necessary to treat them with hydrogen but that it is sufficient to mix the salt with a fatty oil, and to heat the mixture, to produce a substance possessing catalytic properties. Thus the fatty acid salts of nickel, cobalt, iron or

\* British Patent Nos. 21,041 and 23,873, 1913. J. S. C. I., 1916, 1122; Chem. Abs., 1917, 219; British Patent No. 29, Sept. 17, 1913; Chem. Abs., 1917, 105; see also British Patent No. 4,144 of 1913; Holland Patent No. 2,322, Feb. 15, 1915 to Wimmer and Higgins.



copper may be heated in a protective neutral or inert medium such as a fatty body or oil.

The reaction may be carried out by merely mixing the organic metal salt with the medium or fatty body and while heating the mass, submitting it to sufficient mechanical mixing to maintain it at a uniform temperature throughout. With such treatment the mass blackens and the degree of this blackening may be taken as a guide as to the extent to which the catalytic body is produced. The temperatures required will be determined accordingly, being varied according to the salt used, the lowest temperature at which treatment can be conveniently carried out being best. As the temperatures are relatively high (from 200° to 260° C.) it is recommended to perform the reaction in a vessel from which air is excluded thus preventing undesirable oxidation of the fatty body. By passing through the mixture a stream of indifferent gas, such as carbon dioxide or nitrogen, contact with air is avoided. Mechanical stirring may be employed in such cases but if the stream of indifferent gas be sufficiently rapid this is not necessary.

In heating the reaction mass, it is desirable to use an oil bath, as the development of local superheating may produce side reactions, tending to diminish the activity of the catalytic mass.\*

On passing hydrogen through nickel formate and gelatin in glycerine, at 200 to 210° C, colloidal nickel is obtained.\*

A volatile organic acid of the nature of formic acid has been found by Higgins † to accelerate catalysis. The formic acid may be used as a liquid or in the state of vapor. It may be sprayed into the substance to be treated or into the vessel in which the process is conducted or carried into the reaction mass in vapor form in the hydrogen employed, the object in each case being to insure that catalysis may take place in the presence of the free volatile organic acid. By the action of formates and similar compounds reduction is effected, without heating under pressure. For example, cottonseed oil may be reduced by heating at 210° C. with 60 per cent of its weight of nickel formate, air being excluded.‡

The oxalates, tartrates and acetates of nickel and iron are mentioned as catalyzer raw materials in the preparation of a catalytic body used by Valpy and Lucas § in the cracking of hydrocarbon oils.

Finely-divided copper prepared by reduction of copper salts, such as the nitrate or carbonate or organic salts which, on heating, evolve indifferent gases, e.g., copper formate or oxalate, is used for the reduction of nitro compounds. These salts may be heated alone or with ammonium carbonate and when necessary, a reducing gas—

\* Kelber, J. Ind. Eng. Chem., 1918, 396.

† U. S. Patent No. 1,211,704, January 9, 1917.

‡ British Patent No. 4,665, Feb. 23, 1914; J. S. C. I., 1916, 317; see also British Patent No. 23,377, of 1912; J. S. C. I., 1913, 989.

§ British Patent No. 5847, March 7, 1914.

hydrogen or carbon monoxide—is passed over the catalyzer raw material at a temperature below red heat to form the metal. The copper may be supported on a pumice, asbestos, kieselguhr or other carrier.

Activators for the copper catalyst are recommended. Alkali compounds, magnesia and alumina are effective. When employing copper formate, no treatment with a reducing gas is necessary. Reduction is best carried out at about 300° C. In some cases copper oxide is formed as an intermediate compound. An excessive temperature gives a catalyzer which deteriorates too rapidly in use.

This form of catalyzer affords good results in the reduction of aromatic nitro compounds at temperatures around 200° C. yielding the corresponding amines in a satisfactory state of purity. The contact material remains active indefinitely.\*

**Richardson** † aims to prepare active catalytic metal, or compounds, at a comparatively low temperature and in a colloidal condition or in a fine state of suspension approaching the colloidal condition, in oils or fats.

In order to bring about this result he uses a salt or compound of the desired metal, which may be copper, cobalt, nickel, or iron, selecting a salt which is soluble in oil or fat, and dissolves it in the oil or fat, using heat if necessary. In order to reduce the active metal from the solution so obtained, a reducing substance such as hydrogen is applied and reduction in the cold or by means of heat and under ordinary atmospheric pressure or higher pressures, is brought about. As suitable oil-soluble metallic salts for the purpose, the metallic salts of the fatty acids are recommended.

The fat or oil in which the reduction with production of active catalyst is to be brought about is placed in a suitable vessel and to it is added from 1 to 50 per cent of a metallic soap or a metallic salt of one of the higher fatty acids, for example, nickel oleate, which is dissolved by means of heat. A suitable reducing agent, which may be hydrogen, under pressure or not, is introduced and solution and reducing agent are thoroughly intermixed by agitation. At the end of the operation, the nickel or other metal is obtained in a colloidal highly active condition or in a state of extremely fine subdivision approaching the colloidal condition, and can then be used to bring about many chemical reactions such as the addition of hydrogen to unsaturated fatty acids and fats. In or after reducing the nickel soap with hydrogen, the hydrogen also tends to saturate the oil.

According to **Hausmann** ‡ the effective hydrogenation of unsaturated substances is obtained by the use of a basic compound of a suitable metal (for example, copper, nickel, cobalt, and other non-

\* *Zeitsch. angew. Chem. Referat.*, 1915, 212; German Patent No. 282,568.

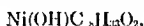
† U. S. Patent No. 1,151,718, August 31, 1915.

‡ U. S. Patent No. 1,145,480, July 6, 1915, Canada, 157,396, August 18, 1914.

noble metals), with a fatty acid soluble in the fatty compound to be treated, such, for example, as oleic, stearic, or like acid.

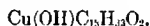
These metallic soaps dissolve in the melted fats or oils, and, on passing hydrogen through the mixture (at a temperature between 100° and 180° C.) a colloidal metallic hydride is formed that is regarded as the active agent in the reducing or hydrogenating reaction. The hydride exists in the mixture as long as there is free hydrogen present. Small additions of such a metallic soap are sufficient to reduce large quantities of the unsaturated materials. The same fatty acids as exist (usually as glycerides) in the compounds to be treated are preferably employed to form the basic metallic compound used for catalysis. The conversion of the basic metallic compound into an active catalyzer, when dissolved in the fatty material, takes place gradually in the hydrogen atmosphere at temperature above 100° C. and a higher temperature of from 160° to 180° C. is recommended in practice. At this temperature copper or other hydride is obtained in colloidal condition.

As an example of the process the following may be taken: 500 parts by weight of raw soya-bean oil are mixed with 0.4 per cent of the basic oleate of nickel:



and the mixture is exposed at about 160° C. to the action of hydrogen by any of the well-known methods until the desired degree of hardening is attained.

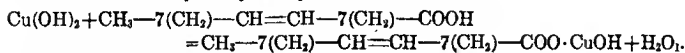
In using a basic oleate of copper



dissolved in the fat and uniformly distributed throughout the whole mass, the compound is acted upon by hydrogen with the formation of water and the mass becomes dark brown. At this stage the freed hydroxyl group probably plays a part in the formation of a copper hydride. By alternate formation and decomposition of this colloidal copper hydride the hydrogen is rendered active, converting the unsaturated fatty compounds into saturated, for instance the oleic acid into stearic acid. Analogous reactions occur with the various metallic compounds which may be employed in accordance with this invention. In no case is the metal itself produced or its oxide, as in some of the prior processes, except at the end of the reaction, when free hydrogen is eliminated to gradually decompose the hydride.

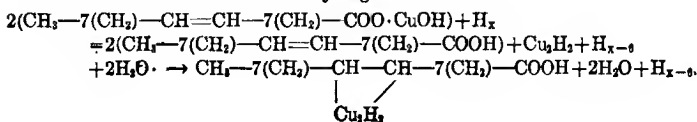
The reactions which occur may be given approximately by the following equations:

Formation of the primary catalyst



that is, basic copper oleate.

The reaction of this oleate with hydrogen



The resulting products are



A process for converting unsaturated fatty acids into saturated compounds similar to the foregoing is described by **Mellersch-Jackson**\* according to which a basic heavy metal salt of a fatty acid of high molecular weight is dissolved in, or intimately mixed with, the substance to be treated, and the material hydrogenated between 100° and 180° C. Basic oleates of nickel and copper are mentioned.†

A catalyzer is prepared by **Thieme** and **Geitel**‡ by heating a mixture of nickel nitrate and an organic salt of nickel. The latter may be prepared by the moderate oxidation of glycerine with nitric acid and subsequent neutralization with nickel carbonate. The compounds of other metals also may be used.

They observe § that the property of "emulsifying" possessed by this form of catalyzer permits the employment of a very simple apparatus and hydrogenation is effected at low temperatures. (140° to 150°.) The process is stated to possess the advantage over former methods in that a metal oxide catalyzer or a metal catalyzer can be produced directly, so that a reduction of the catalyzer in a current of hydrogen is not necessary. Pure nickel glycerate need not be used, as a mixture of nickel salts can be used which is obtained by moderate oxidation of glycerol and subsequent neutralization with nickel carbonate. For example, 3 parts of glycerine of 33 per cent strength are mixed with 2.5 parts of 62 per cent nitric acid. Some potassium nitrite solution is added as catalyzer. The mixture is allowed to stand for three to four days at a temperature of 25° to 30°. The solution is then heated to 90° and after cooling, water is added until the original weight is regained; 1 cc. of the solution must then neutralize 40 to 42 cc. 0.1 N alkali. The product of the reaction is then neutralized with nickel carbonate. For the production of a metal catalyzer 0.6 parts  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  is added, together with a pulverulent inorganic substance, e.g., pumice stone or clay, and the product is evaporated to dryness and decomposed by heating with exclusion of air. To obtain the oxide catalyzer, 3 parts of  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  are added, and the mass is evaporated to a syrupy consistence and decomposed by heating.

The application of nickel oleate in hydrogenating oils, as described by **Ellis**|| involves, in one form, the thermal decomposition of the oleate in an oily vehicle. Beside nickel oleate any suitable metallo-organic compound, especially one soluble in oil and consisting of a

\* British Patent No. 21,477, September 23, 1913.

† J. Ind. Eng. Chem., 1915, 459.

‡ Seifen. Ztg., 1915, 478.

§ German Patent No. 292,894, December 3, 1913; Chem. Abs., 1917, 1530; J. S. C. I., 1916, 932.

|| U. S. Patent No. 1,217,118, February 20, 1917.

metal united to a weak organic acid may be used as a source of catalytic material.\*

By heating these metallo-organic compounds decomposition occurs setting free the catalytic material in a state of extreme subdivision and sometimes forming a colloidal solution. When the catalyzer has been prepared in this manner, it is admixed with the oil that is to be hydrogenated and hydrogen is introduced. In those cases where the metallic catalyzer tends to dissolve in an acid fatty body to form a metallic soap, the temperature during hydrogenation may be maintained at a point above that at which the soap is unable to exist, or if previously formed may be decomposed. A temperature of about 10 degrees above the decomposition point is recommended.

Details of preparation of catalyzers by the thermal decomposition of nickel oleate or other organic compound of nickel are indicated by Ellis.† A catalyzer may be made by the reduction of nickel acetate in hydrogen.‡ A mixture of nickel formate and nitrate when heated gives catalytic nickel material.§ Ellis proposes to make a catalyzer concentrate by decomposing in oil, an excess of a decomposable compound of nickel.|| Nickel carbonyl may be used in this case.

In the hydrogenation of oils with colloidal nickel catalyzers, Ellis recommends that especial care be taken to free the hydrogen gas employed, from chlorine.¶

A catalyzer for hydrogenating oils is prepared by the **Bremen-Besigheimer Oelfabriken,\*\*** by impregnating kieselguhr or asbestos with a solution of nickel acetate, adding a limited quantity of oil and heating in a vacuum at a temperature between 150 to 200° C. Finally hydrogen is passed through the mixture.

Catalysts such as finely divided reduced nickel, cobalt, manganese, copper, etc., for hardening fats are prepared by **Soc. de Stearinerie et Savonnerie de Lyon and Berthon,††** from metallic oxides by reduction at about 250° C. in a neutral liquid medium such as paraffin, vaselin or heavy petroleum oil with the addition of 0.25 to 0.5 per cent of stearic acid. The material is placed in vertical tubes and heated to about 250° C. The metallic oxide is then added and hydrogen is injected. Perforated plates are arranged in the tubes. The catalytic metal is obtained after about 2.5 to 3 hours and the liquid medium is separated by centrifuging.

\* Patent No. 1,217,118 was involved in an interference with the Wimmer and Higgins Patent No. 1,081,182 described on pages 47-8 and priority was awarded to Ellis for this use of organic compounds of nickel in the hydrogenation process. In an interference with Hausmann, priority was also awarded Ellis and the application on which Letters Patent No. 1,145,480 was issued to Hausmann July 6, 1915, was involved in a like interference.

† U. S. Patent No. 1,251,201, Dec. 25, 1917.

‡ Ellis U. S. Patent No. 1,251,203, Dec. 25, 1917.

§ U. S. Patent No. 1,251,204, Dec. 25, 1917, to Ellis.

|| U. S. Patent No. 1,251,202, Dec. 25, 1917.

¶ U. S. Patent No. 1,184,086, May 23, 1916.

\*\* German Patent 304,043, August 18, 1912.

†† British Patent 107,004, May 19, 1917 and 107,969, June 25, 1917; J. S. C. I., 1918, 421 A and 462 A.

## CHAPTER VIII

### THE BASE METALS AS CATALYZERS.—Continued

#### NOTES ON NICKEL OXIDE CATALYZERS

Bedford and Erdmann\* assert that metallic oxides can be produced in an extremely finely-divided and voluminous form by preparing a concentrated aqueous solution of a nitrate, mixing the same with an organic compound which is soluble in water and rich in carbon and subsequently decomposing by heat. A strong evolution of gas takes place during the combustion of the organic substance with the nitrate and the metallic oxide swells up to a large volume, assuming the form of a dust, while the whole of the carbon present in the organic compound is removed by the combustion. On reducing with hydrogen at 200° to 300°, the metallic oxides prepared according to this method can be converted into the corresponding voluminous and catalytically active metals.

*Example:* Nitric acid of specific gravity of 1.42 is diluted with an equal volume of water and to the diluted acid pure metallic nickel is added. When the resulting reaction is completed, the whole is heated to boiling for about two hours in the presence of an excess of nickel in order to neutralize completely the nitric acid present and to precipitate any iron which may occur as hydrated oxide of iron. The clarified nickel nitrate solution is evaporated until its specific gravity is 1.6 and for each liter of this liquid (corresponding to 250 g. of nickel) are stirred in 180 g. of powdered cane sugar. This solution is run in portions into a muffle of any suitable construction heated to a dull red heat and the heating of each portion is continued until no more fumes escape. The voluminous nickel oxide thus formed is removed from the muffle by means of a scraper and a fresh portion of the solution run in.

By means of the process, cobalt oxide, iron oxide and other oxides of the heavy metals which may be used for catalytic purposes, can be produced in a light voluminous and catalytically active form and are well adapted both in the form of oxide and in the form of metal

\* U. S. Patent No. 1,200,896, October 10, 1916.

as catalytic material for adding hydrogen to unsaturated organic compounds. Other forms of sugar, or starch, dextrin, gum arabic or tartaric acid may be used in place of cane sugar.

**Normann** \* states that up to the present time there is no positive proof of the existence of nickel suboxide in catalytic nickel material. The reaction of the reduced catalytic substance with phosphomolybdic acid as employed by Erdmann is by no means a specific test for nickel suboxide but is exhibited by many reduced bodies such as finely-divided metallic nickel. The method of testing electrical conductivity used by Erdmann is not proof of the absence of metallic nickel †. Erdmann's contention that the blackening and fine distribution of the catalyzer in oil when under initial reducing conditions indicates the presence of suboxide of nickel is regarded as groundless. Finely-divided metallic nickel is black and it is known that nickel carbonyl when decomposed in oil yields an inky black liquid. Normann very pointedly observes that he might just as well claim the blackening was a "proof" of the formation of metallic nickel as of the suboxide.

The failure of Bedford and Erdmann to observe the formation of metallic nickel when employing the oxide is due to erroneous methods of examination, according to Normann and Pungs.‡ It is, of course, of importance to the further development of the hydrogenation process to settle the question whether the metal or its oxide is the real hydrogen carrier, Normann and Pungs endeavored to find a reliable method of determining metallic nickel and investigated the products obtained with nickel oxide, the carbonate, also the formate and other organic salts of nickel. The results obtained with nickel oxide likewise apply to these nickel salts.

For the experimental work 300 cc. round-bottomed flasks having a gas inlet tube at the bottom were used. The bulk of the flask was almost completely immersed in an oil bath heated to 255° C. Various fatty oils were hydrogenated, including olive, linseed, sesame, whale and refined cotton oil which had been blown with superheated steam under diminished pressure. The kind of oil employed made no difference as regards the formation of metallic nickel; 100 g. of oil were heated in the flask to 200° C. and hydrogen at the rate of 2 liters per minute were passed through the oil, thereby causing brisk agitation. One gram of nickel oxide was then added and the temperature raised to 255° C. Small samples were withdrawn from time to time and the melting-point determined. When a melting-point of 45° C. was reached, which usually required two to three hours time, the nickel material was collected and tested for the presence of the free metal. Both pure and technical nickel oxide were examined and the different grades of the oxide were found to be more or less efficient in hardening oil and substantially alike as regards the formation of free nickel.

**Determination of Electrical Conductivity.** The terminals of a small dry battery were connected, each to a metal plate, so that the circuit would be closed on

\* *Seifen. Ztg.*, 1915, 47 and 191.

† See Normann and Pungs, *Chem. Ztg.*, 1915, No. 6 and 7/8.

‡ *Chem. Ztg.*, 1915, 29.

contact of the two metal plates. In the circuit was placed a galvanometer or an electric bell. A sheet of mica with an opening 1 centimeter square was placed between the plates, thereby insulating them. In testing conductivity a small amount of the powder was placed in the square opening, in contact with a metal plate and the second plate pressed on to the mass. The deflection of the galvanometer indicates the relative conductivity and when high, enough current may pass to ring the bell. Lack of deflection of the galvanometer is, however, no indication of the absence of metallic nickel. A catalyzer used by the Oelwerke Germania of Emmerich and prepared by reduction with hydrogen of nickel material supported on an inorganic non-conducting pulverulent carrier did not prove to be a conductor. When nickel oxide is used for oil hardening, and the resulting black powder separated by deposition and washing with benzol, in some cases the used catalyzer conducts electricity, while in other cases it does not exhibit this property. Doubtless the conductivity is dependent on the actual metal content of the powder. It is conceivable that each particle of nickel oxide is not at once fully reduced to the metallic state but that superficial reduction first occurs and by continued contact with hydrogen, the content of free metal increases. The dependence of the degree of conductivity on the duration of exposure to hydrogen and consequent variation in metal content is shown in the tables below. The percentage of nickel is calculated on the amount of hydrogen liberated by dilute sulphuric acid.

## CONDUCTIVITY OF REDUCED NICKEL OXIDE

## KAHLBAUM'S NICKEL OXIDE IN COTTONSEED OIL

Time of Hardening	Total Nickel in Used Catalyzer	Free Nickel in Used Catalyzer.	Iodine No. of the Hardened Fat.	Conductivity.
Two hours. . . . .	79.4	12.7	63	none
Two hours, fifty minutes.	85.2	41.2	21.2	good
Four hours . . . . .	.....	.....	9.7	good
Seven hours.....	88.1	53.0	3.85	good

Thus it appears that the conductivity becomes manifest between 12 per cent and 41 per cent of free nickel. The nickel content of the above-mentioned commercial catalyzer (Oelwerke Germania) of a non-conducting nature lies between these limits.

Linseed oil was used in the 1 per cent nickel oxide tests, and in all the others cottonseed oil was employed.

By a magnetic method of separation similar to that used by Erdmann \* who obtained negative results, Normann and Punga succeeded in isolating the better conducting portions of catalytic material having a low content of free nickel. The oil and catalyzer mixture after treatment with hydrogen, was cooled to 140° C. and a strong electro-magnet moved about in the oil thus attracting the nickel particles which were removed and washed with benzol. The nickel material was collected with the magnet and introduced into fresh benzol and the operation repeated several times. A fractionation of metallic nickel from nickel

\* Journ. Prakt. Chem., 1913, 437.



oxide, although the latter is somewhat magnetic, is thus obtained. The nickel powder is well washed with ether and dried in a drying oven. It is then ready for a conductivity determination.

#### CONDUCTIVITY OF REDUCED NICKEL COMPOUNDS.

Catalyzer Material	Melting-point of Resulting Fat	Conductivity.
Nickel oxide, $\frac{1}{2}$ per cent Kahlbaum.....	28	none
	32 2	none
	45.6	good
	53 6	good
Nickel oxide, 1 per cent Kahlbaum.....	liquid	none
	salve-like	none
	27.	good
	46 2	good
Nickel oxide, Merck.....	45 5	good
Nickel carbonate.....	49 8	noticeable
Nickel hydroxide.....	45 9	noticeable
Nickel formate, 5 per cent.....	.....	good
Nickel formate, 3 per cent.....	45.5	good
Nickel formate, 1 per cent.....	.....	good

The powder is pressed between the metallic plates preferably gently rubbing to secure good contact. Too violent rubbing tends to reduce conductivity, which is explained on the supposition that the particles by partial reduction acquire a skin of metallic nickel and these particles show metallic conductivity. If crushed, a mixture of conducting and non-conducting material is produced and the latter obstructs the flow of the current.

Extremely fine metal powders conduct electricity poorly or not at all. Nor-mann and Pungs frequently observed a lack of conductivity in products which were prepared under conditions inevitably yielding a substantial proportion of free metal, and which, indeed, afforded a positive test for nickel by the carbonyl reaction. This was noted particularly when using nickel carbonate. On bringing a magnet near a mass of warm fat containing the products of the action of hydrogen on the carbonate, no particles were attracted, but a peculiar light reflex was noted which changed as the magnet was moved about, showing magnetic orientation of the suspended particles. On microscopic examination, these supposedly granular particles were found to be rod shaped. Evidently these minute rods became magnetically polarized and changed position in the oil to accord with the pole of the magnetic source presented. The product was allowed to stand in oil overnight and the following morning it was treated with hydrogen for one-half hour at 200° C. Then it was found that the fine particles had formed into aggregates which were easily attracted by the magnet and conducted electricity.

A qualitative test of conductivity was not deemed sufficient proof of the presence of free metal, as metallic oxides, such as nickel oxide, even when perfectly dry, show a slight degree of conductivity. By strongly rubbing nickel oxide between the pole plates a considerable deflection of the galvanometer

frequently was noted. Metallic oxides appear to contain particles of relatively good conductivity which contact on rubbing and provide conducting zones. Normann and Pungs made a number of determinations of electrical resistance with the Wheatstone bridge on various oxides, before and after employment in the hardening process. A centimeter square opening in a mica plate between two metal plates was used in these as in the preceding determinations.

## MEASUREMENTS OF RESISTANCE IN OHMS

NICKEL OXIDE (iv). KAHLBAUM.		NICKEL OXIDE (ous) KAHLBAUM.		NICKEL OXIDE MERCK		Nickel Carbonate After Fat Hardening.
Before	After	Before	After	Before	After.	
8000	2 1	over	3	over	15	1
8500	2 5	50,000	1.5	50,000	18	
900	20.	....	100	....	100	
9000	70.	....	90	....	10	
.....	30.	....	20	....		
.....	0.7	....	15			
.....	0.8	....	16			

These measurements show a decided difference in conductivity before and after fat hardening.

Bedford and Erdmann have referred to a suboxide of nickel reported by Moore \* in support of the contention that the suboxide is formed in the hydrogenation process. Normann and Pungs prepared a suboxide according to Moore's procedure and found it lacking in conductivity. However, after using this compound for oil hardening the conductivity was excellent indicating reduction to the metallic state.

**Analytical Determination of Free Nickel.** The analytical determination returns a higher content of nickel than the conductivity indicates, and invariably more nickel is found than would correspond to the suboxide formula. The following examination was made:

1. Two hundred and fifty grams of olive oil were hardened at 250° C. using 2.5 g. of nickel oxide prepared from the nitrate. The fat melted at 55.2° C. and possessed an iodine number of 31. The catalyzer was allowed to settle and was repeatedly washed with benzine and benzol. The last portions of the solvent were removed with carbon dioxide. To remove occluded hydrogen the catalyzer was exposed for one hour to a vacuum of 1 mm. mercury. The nickel product was treated with sulphuric acid and the evolved hydrogen measured. Some fatty material separated when the acid was added and correction was made for this.

Weight of substance taken.....	0.2313 g.
Fat separated.....	0.1204
Fat free catalyzer.....	0.1109 g.

\* Chem. News, 1893, 68, 295; 1895, 71, 81.

With sulphuric acid, 36.4 cc. of hydrogen at 23° C. and 756 mm. were evolved corresponding to a content of 77.4 per cent free nickel. If the formula of the suboxide is regarded as  $\text{Ni}_3\text{O}$  and there action as  $\text{Ni}_3\text{O} + 3\text{H}_2\text{SO}_4 = 3\text{NiSO}_4 + \text{H}_2\text{O} + 2\text{H}_2$ , then the hydrogen actually found represents a content of 125 per cent nickel suboxide or 114.6 per cent total nickel. If the formula of the suboxide is considered as  $\text{Ni}_2\text{O}$  \* the results calculated on the hydrogen gas evolved would be 173.5 per cent  $\text{NiO}$  and 152.7 per cent total nickel, all of which figures are, of course, impossible.

2. One hundred grams edible sesame oil were hardened with nickel oxide (ous) Kahlbaum at a temperature of about 255° C. to a melting-point of 48.1° C. The catalyzer was dissolved in sulphuric acid, the hydrogen measured and the total nickel determined electrolytically. Results: 0.1706 total nickel, 62.1 cc. hydrogen at 26° C. and 774 mm. corresponding to 86.5 per cent of nickel. If figured as  $\text{Ni}_3\text{O}$  the nickel content would be 128.7 per cent.

3. Five hundred grains sesame oil were hardened with 5 g. nickel oxide (ous) Kahlbaum to a melting-point of 52° C. The catalyzer was removed by means of a magnet. On treatment with sulphuric acid some fatty matter and green nickel oxide remained undissolved. The hydrogen evolved corresponded to 76.8 per cent nickel but if a suboxide  $\text{Ni}_3\text{O}$  were assumed to be responsible for this amount of hydrogen, 124.6 per cent of the suboxide would be required.

4. Five hundred grams of sesame oil were hardened to a melting-point of 53.5, using 5 g. nickel oxide (ous) Kahlbaum and the catalyzer treated as in determination No. 3. The hydrogen given off was equivalent to 71.4 per cent nickel. Correction was made for undissolved nickel oxide and fatty residue. Calculated to  $\text{Ni}_3\text{O}$ , the percentage of the latter would be 115.6. Normann and Pungs consider these determinations to fully establish the fact of formation of metallic nickel in all cases, even if it be assumed that some suboxide is formed. They find, however, no basis for such an assumption.

**The Nickel Carbonyl Test for Metallic Nickel.** In testing nickeliferous catalyzers for free nickel by the carbonyl reaction Normann and Pungs † note that certain precautions must be observed. The greatest care should be taken to have the carbon monoxide employed very pure and thoroughly dry. Normann and Pungs prepared the monoxide by allowing concentrated formic acid to drop into concentrated sulphuric acid heated by a water-bath. The gas was dried by passago through sulphuric acid and then over soda lime and solid caustic soda.

The carbonyl reaction is extraordinarily sensitive to the presence of air. Simply by pouring the hardened fat and catalyzer from one vessel to another, suffices to nullify the reaction. Accordingly, after hardening, the fat and catalyzer is cooled to 90° to 100° C. in a weak current of hydrogen. Then the vessel is placed in a water-bath at 90° to 92° C. and the hydrogen replaced by carbon monoxide. The gases leaving the reaction flask are passed through a hard glass tube which is heated at one point. Nickel carbonyl is decomposed and forms a mirror on the glass walls in the heated zone. To obtain good adherence of nickel the tube must be thoroughly clean. The separation of nickel is not quantitative. Some carbonyl escapes decomposition in the heating zone, as may be shown by igniting the issuing gas. The flame is colored yellow or if the amount of car-

\* Bellucci and Correlli, *Z. anorg. Chem.*, 1914, 88.

† *Chem. Ztg.*, 1915, 41.

bonyl is extremely minute the color is a pale blue. Only a few minutes suffice to secure a heavy nickel mirror.

## NICKEL CARBONYL REACTION ON CATALYZERS.

Oil.	Catalyzer.	Melting-point of the Hardened Fat.	Nickel Mirror.
Cotton oil.....	5 per cent basic nickel formate	50.8	marked
Cotton oil.....	5 per cent basic nickel formate	51.2	marked
Cotton oil.....	1 per cent nickel carbonate	49.8	marked
Cotton oil.....	$\frac{1}{2}$ per cent oxide (Erdmann)	46.2	marked
Pure linseed oil.....	$\frac{1}{2}$ per cent oxide (Erdmann)	42.4	marked
Whale oil.....	$\frac{1}{2}$ per cent oxide (Erdmann)	46.8	marked
Linseed oil.....	$\frac{1}{2}$ per cent oxide (Kahlbaum)	42.5	marked
Linseed oil.....	$\frac{1}{2}$ per cent oxide (Merck)	40.6	marked
Linseed oil.....	$\frac{1}{2}$ per cent oxide from nitrate	40.6	marked
Linseed oil.....	$\frac{1}{2}$ per cent oxide (Kahlbaum)	40.2	marked

If hydrogenation is allowed to progress to a lesser degree, the mirror appears with the carbonyl test. For example, olive oil was hardened to a melting-point of only 17° C. and a positive test for nickel was obtained. If fat hardening is carried out at a temperature below that prescribed by Erdmann, or not over 230° C., blackening of the green nickel oxide does not occur, the color changing only to a greyish green. The iodine number of olive oil, after 3½ hours hydrogenation under these conditions, fell but one or two units. The carbonyl test was positive although very weak. A blank test with the same nickel oxide in fresh oil and without treatment with hydrogen, maintained at 90° C., while carbon monoxide was passed through, showed that nickel oxide was not reduced by the monoxide under these conditions.

Since Erdmann has suggested that the reduction of nickel oxide may be brought about by aldehydes contained in the oil, Normann and Pungs tested the reducing effect of formaldehyde and benzaldehyde, two of the most powerful reducing aldehydes. They heated a mixture of edible oil, aldehyde and nickel oxide on an oil bath at 225° C., without introducing hydrogen. No reduction of the oxide was noted; in one case, olive oil, benzaldehyde and green nickel oxide were heated to about 250° for four hours, using a reflux condenser; but no blackening of the oxide was perceptible. The likelihood of reduction by the aldehydes of fatty oils, therefore, appears to be remote.

In the table below the results of the carbonyl reaction at a temperature of 50° C. are given when employing olive oil of iodine No. 82, freed from aldehydes by the silver nitrate method of Beechi, and hydrogenating at a temperature of 250° C. in the first four tests and at 230° C. in the remaining tests.

Thus, at 50° C. as well as at 90° C., the carbonyl reaction is obtained from catalyzer in oil. Even at 30° C. the carbonyl is slowly formed. At 30° C. the necessary contact of the monoxide with the relatively thick oil is difficult to bring about.

An endeavor was made to make the carbonyl test a quantitative one. To this end, the glass tube in which the nickel carbonyl was decomposed, was filled

with fragments of porcelain and was heated in two or more places. It was then noted whether or not at the place of heating most remote from the point of entry of the carbonyl, any nickel was deposited. The exit gases were ignited and the color of the flame noted. It should be a pure blue. From 1 g. of catalyzer held at a temperature of 90° C. for four hours 0.05 g. of nickel were obtained. A second test conducted for four days gave 0.07 g. nickel. Even then the reaction had not been completed. Nickel carbonyl was still being formed in the oil.

#### NICKEL CARBONYL FORMATION AT 50° C.

Catalyzer.	Melting-point of the Hardened Fat.	Iodine No.	Carbonyl Test.
1 per cent nickel oxide (ic) Kahlbaum....	15.5	68.4	Heavy nickel mirror
1 per cent nickel oxide (ic) Kahlbaum....	49.6	37.1	Heavy nickel mirror
1 per cent nickel oxide (ous).....	27.0	67.4	Heavy nickel mirror
1 per cent nickel oxide (ous).....	49.8	38.0	Heavy nickel mirror
1 per cent nickel oxide (ous) Temp. 230°...	Liquid	78.0	Distinct mirror
1 per cent nickel oxide (ous) Temp. 230°...	Liquid	79.0	Weak but distinct mirror

If the residue of nickel in the oil is regarded as negligible, Normann and Pungs assume the hardening to have been carried out with a catalyzer consisting of about 7 per cent of metallic nickel on upwards of 90 per cent of nickel oxide serving as a carrier. The question then arose as to the possibility of so small a proportion of nickel effecting the degree of hydrogenation noted. Normann and Pungs regard the question as answered as a result of their practical experience. It is stated that a catalyzer of this composition, when carefully and skillfully prepared, gives good results not only in the laboratory but also on the large scale. From repeated use more nickel is likely to be reduced as a result of the continued contact with hydrogen.

A nickel-kieselguhr catalyzer was prepared by reduction at 450° to 500° C. at which temperature the existence of a suboxide is regarded as entirely excluded. The content of free nickel, calculated from a determination of the volume of hydrogen evolved by sulphuric acid was 4.2 per cent. By the addition of only 1 per cent of this catalyzer to refined sesame oil, the melting-point was raised to 45° C. on hydrogenating for one hour. Normann and Pungs do not record the amount of nickel computed from the mixing formula of this catalyzer so that it does not appear whether or not this calculated proportion checks with the result of the hydrogen evolution determination.

In every instance, the catalyzer material, which before hardening, did not contain free metal, after hardening, showed the presence of the metal, hence, irrespective of the question of formation of nickel suboxide or other assumed reduction product intermediate nickel oxide and the metal, it is concluded that fat hardening does not occur in the absence of the free metal and that some substance other than the free metal is an active catalytic agent, as contended by Erdmann, has not been proven.

**Metallic Nickel vs. Nickel Oxide.** In the discussion between Normann and Erdmann over nickel borate certain comments by the latter\* are of interest in spite of the controversial attitude of Erdmann. He states:

(1) Through mere heating of finely-divided, freshly-reduced nickel in oil with or without the presence of hydrogen an inky black liquid never is formed.

Considering the conditions under which reduction of a higher oxide of nickel in oil takes place, nickel suboxide has at least an equal chance of forming as metallic nickel and it is logical to conclude that the suboxide is responsible for the black coloration.

(2) Dark-colored suspensions of colloidal nickel may be obtained by electrical comminution of the metal in oil. When this suspended material is separated it is found to conduct electricity like a metal quite unlike nickel oxide suspensions.

(3) As hydrogen carriers, such colloidal suspensions of metallic nickel are practically of no value. For this reason Shukoff's nickel carbonyl process† has not come into use.

Erdmann then proceeds to criticize Normann's view that the activity of a metallic catalyzer resides in an important measure in its degree of subdivision especially the statement by the latter that "For this reason, carriers for the metallic nickel have come into use. Thus, it is possible to prepare metallic catalyzers which are almost without activity, and again, others which have extraordinary efficiency." Obviously, Erdmann states, the fine nickel powder obtained by reduction in a current of hydrogen as set forth in the Leprince and Siveke Patent No. 141,029 belongs to the first category—the almost inactive class. But whether the fine subdivision alone of the catalytic is responsible for its high degree of activity is a consideration which Erdmann declines to discuss.

The greater activity of once used nickel oxide catalyzer as compared with the original oxide is due to the formation of metallic nickel, according to Oelwerke Germania.‡ By repeated use the oxide catalyzer operates satisfactorily at the same temperature as the free metal catalyzer and the high temperature of 250° required in the first instance is necessary, not for hardening, but for the formation of free nickel.

The manufacture of nickel oxide masses from granular nickel compound such as the carbonate, by igniting in a reducing gas atmosphere is described by Hoyer.§ For the production of the granular nickel compound pulverized nickel carbonate is moistened with water so that it bakes together, and after drying is cut into grains. These grains are rounded off, compacted and after drying, are reduced in illuminating gas. The ignition must not be too strong, since otherwise the grains become too hard.

Paal and Brunjes state that sodium protalbinat and lysalbinat exert only a relatively slight protective action on sols of nickel hydrate and that it is impossible to obtain sols of high nickel hydrate content by their use. The preparation of stable hydrosols containing 6 to 10 per cent nickel hydrate is described.||

\* Seifen. Ztg., 1915, 288.

† German Patent No. 241,823.

‡ Seifen. Ztg., 1914, 645.

§ German Patent No. 277,743, July 17, 1913; Chem. Abs., 1915, 761.

|| Chem. Abs., 1914, 3275; Ber., 47, 2200-2.

**Robson notes** \* that the use of nickel oxide as a catalyzer is defended by the *Industria Saponica* of Milan, which asserts that the use of metallic nickel can never achieve commercial importance. This curious pronouncement is made on two grounds. One is that the claim as to the effect of impurities in the oil upon the nickel is correct, as even if the hydrogen used is chemically pure, traces of albuminous bodies left in the oil by defective refining check the efficiency of the nickel materially, causing the action to be slow and giving a diminished output, with a largely increased amount of nickel. The other ground is that the activity of the metal is diminished seriously even if the fat to be hardened is pure, by the presence of impurities in the hydrogen, especially traces of chlorine or of sulphuretted hydrogen.

For preparing a catalyzer for hydrogenation of oils and fats, the **Suzuki-Shoten Co.**† treats corn husks, sawdust, or insoluble organic substances rich in carbon with a mineral acid and works the mixture into a paste with nickel, iron or copper material. This paste is ignited to produce a porous carbon which retains metallic oxides in a highly active state.

British Patent No. 29,981 of 1912 for An Improved Process for the Preparation of Saturated Fatty Acids, their Glycerides and other Esters, issued to **Bedford, Williams, Erdmann and Hydroil Limited**, indicates that on further study of the process protected by British Patent No. 29,612 of 1910, it has been found that nickel suboxide is especially suitable as a reducing catalyst for the addition of hydrogen to unsaturated fatty acids or their glycerides. The patentees state that nickel suboxide is one of the lower oxides of nickel and its formula has not yet been definitely settled. Muller ‡ and Glaser § ascribe to it the formula  $\text{Ni}_2\text{O}$ , but Thomas Moore, who has more than anyone else examined this compound in detail, gives it the formula  $\text{Ni}_2\text{O} \cdot 2\text{H}_2\text{O}$ .||

Although its formula is uncertain the suboxide possesses characteristic properties. It is strongly magnetic, gives off hydrogen on treatment with dilute mineral acid, evolves nitric oxide fumes even in the cold. While it is distinguished by these properties from all other nickel oxides it is sharply distinguished from metallic nickel in that it possesses no electric conductivity, thus, if a pastille be pressed out of nickel suboxide, the polar ends of two wires be inserted therein and a source of electric energy at an E.M.F. of 24 volts be included in the circuit no current is indicated by a sensitive galvanometer in the circuit even when the wires are only separated from one another by a distance of 1 millimeter.

It is further found that nickel suboxide is characterized by the property of giving colloidal solutions. The red solutions obtained according to Moore on reducing an aqueous solution of potassium nickel cyanide with sodium amalgam or zinc coated with copper or by means of an electric current contain the suboxide in colloidal solution. On allowing these red solutions to stand for some time, black nickel suboxide separates out in a flocculent mass. Oils in addition to water have the power of taking up the suboxide in a colloidal form.

On heating nickel suboxide, prepared according to one of the methods described in literature, with a fat or fatty acid, the nickel suboxide distributes

\* *Drugs, Oils and Paints*, 1914, 211.

† Japanese Patent 31,590, October 4, 1917; *Chem. Abs.*, 1918, 538.

‡ *Poggendorf's Annalen*, 136, 1869, 51.

§ *Zeitschrift für anorg. Chemie*, 36, 18.

|| *Chemical News*, 71, 1895, 81.

itself therein in an exceedingly fine state of division to form a black, inky liquid which passes through any filter unchanged. The same colloidal division takes place if a higher nickel oxide be suspended in a fatty oil and reduced to nickel suboxide by means of a current of hydrogen. This property of colloidal distribution imparts to the nickel suboxide to an extreme degree the power of adding hydrogen to unsaturated fatty acids and their glycerides in a manner similar to that in which the addition of hydrogen takes place by means of colloidal platinum.

In operating the process of British Patent No. 26,912, of 1910, nickel suboxide is stated to be formed to a certain extent when ordinary nickel oxide is employed in the process of hydrogenation. In the present case, however, nickel suboxide is first prepared and is then added to a quantity of the oil which is to be hydrogenated. The advantage derived by this procedure resides in the lower temperature at which the addition of hydrogen takes place. Thus, it is not necessary to heat the oil so strongly as when ordinary nickel oxides are employed.

(A) Sesame oil is heated in a copper vessel with 1 per cent of nickel suboxide to 200° C., and a strong current of hydrogen is passed through the oil. The suboxide immediately forms with the oil an inky liquid and after a few hours the mass solidifies at 46° C.

(B) Ordinary nickel oxide in as finely-divided condition as possible is heated with ten times its weight of cotton oil to 260° C., and a strong current of hydrogen passed through for one hour whereupon the greyish green oxide assumes a black color and distributes itself colloiddally throughout the oil. The mass is allowed to cool somewhat and then run into 200 times its weight of cotton oil which is now hydrogenized at 185° C. After two hours the solidifying point of the mass is about 50° C.

In the prosecution of the application from which U. S. Patent No. 1,026,339, of May 14, 1912, to Bedford and Williams was derived, the statement appears that:

It has never been known to hydrogenize unsaturated compounds with nickel oxide as a catalyzer at any other than very high pressures which render the processes unworkable as commercial processes as is evidenced by the following literal translation of a portion of a paper contributed by S. Fokin in the Journal of the Russian Chemical Society, 1910, page 1074.

"It has been found by V. I. Ipatiew that  $\text{Ni}_2\text{O}_3$ , when used for experiments at high temperatures and pressures, gives, as regards the velocity of the reaction of the hydrogenization of unsaturated compounds, a better effect than metallic nickel reduced from its oxide.\* The participation of some of the lower forms of nickel oxide appeared to be very probable and to explain this unexpected circumstance. But if such explanation is suitable for very high pressures nothing similar is observed at pressures within the limits of ten to twenty atmospheres and at ordinary pressure. The nickel oxide becomes reduced to suboxide and there the matter ends. The hydrogenization of the unsaturated compounds does not take place here."

What is termed a semi-reduced hydrogenation catalyzer is detailed by Ellis,<sup>†</sup> the preparation of which is carried out by the careful

\* Method of Sabatier & Senderens.

† U. S. Patent No. 1,150,480, November 9, 1915.



reduction of nickel oxide or hydrate to effect only partial reduction, ordinarily about one-half of the oxygen being removed, affording an intimate mixture of catalytic nickel combined with nickel oxide or certain of the suboxides. Besides hydrogen, other reducing gases or vapors, namely, water gas, carbon monoxide and the vapor of alcohol, are mentioned.

A catalytically active nickel black is produced by Boyce \* by reducing nickel oxide with hydrogen. The action is stopped before complete reduction takes place, leaving a product which is predominately black.

**Boehrer & Söhne** † hydrogenate unsaturated substances in the presence of a suboxide of the nickel group as catalyst. The substances are treated when in solution or suspension in an alcohol instead of in water.‡ In examples, dihydroquinine is obtained by treating quinine hydrochloride in solution in methyl or ethyl alcohol in the presence of nickel suboxide, and cinnaemyleocaine is hydrogenated when in solution in ethyl alcohol in the presence of the same suboxide.

**Meigen** § defends his former assertion that it is metallic nickel which transfers hydrogen to oils and fats instead of some suboxide of nickel as maintained by Erdmann and Bedford.||

New experiments are described, some in detail, on the hardening of sesame and soya-bean oils at 240° to 280°, using nickel oxides and at 170° to 180° using reduced nickel as catalyzers. Results of tests for metallic nickel, evolution of hydrogen, electrical conductivity and formation of nickel carbonyl are given. Summary: (1) nickel oxide is an active catalyst only when free metal is present. (2) Erdmann's objections to Meigen's former experiments are based on false assumptions. (3) The presence of free metal in used catalyzers is again proved. (4) Lack of electrical conductivity or absence of the carbonyl-reaction are not proof of the absence of free nickel, while positive results with these tests always prove its presence. (5) The specific gravity of catalyzers depends essentially upon organic impurities and proves nothing as regards presence of nickel suboxide. (6) The assertion that suboxide or "suboxide hydride" is formed, is not proved.

The principal results of an investigation made by **Frerichs** ¶ are summarized as follows:

It is solely an assumption of Erdmann and his co-workers that reduction of nickel oxides in oil by means of hydrogen stops with the formation of a suboxide and that such suboxide acts as a hydrogen carrier. The existence of a nickel suboxide is held to be entirely problematical. Equally questionable are

\* Canadian Patent No. 171,436, Aug. 22, 1916; Chem. Abs., 1918, 749.

† British Patent No. 21,948, November 3, 1914; Chem. Abs., 1916, 1407.

‡ See British Patent No. 21,883, 1914; Chem. Abs., 10, 1081.

§ J. prakt. Chem., 92, 390-411, 1915; Chem. Abs., 1916, 1105.

|| Chem. Abs., 9, 3136.

¶ Arch. Pharm. 233, 512, 1915; Chem. Abs., 10, 1441.

assumptions and assertions that hydrated nickel oxides are formed, or that nickel compounds in general can act as hydrogen carriers. It has been demonstrated with certainty, not only through electrical conductivity but also with the carbonyl test, that metallic nickel results during the hardening of fats through application of nickel and other nickel compounds. Thus it has been shown that reduction of nickel oxide in oil by hydrogen does not stop at a suboxide but on the contrary progresses as in an ordinary dry reduction to the metal itself. It is certain that the inability on the part of Erdmann and co-workers to detect metallic nickel by means of electrical conductivity was in the main due to contaminations of fatty acid salts of nickel and other products contained in the samples examined. Thus, Siegmund and Suida failed to detect electrically a content of at least 48 per cent nickel which according to their own analyses must have been present. Erdmann's explanation of the action of nickel oxides as given in a series of tests designed to be comparative cannot be regarded as a proof, since possibility for comparison is excluded under the varied conditions obtaining in metallic nickel reduced in oil and in the dry state. Frerichs further asserts that it must be regarded as proved that, in hardening fat by use of nickel oxide, the hydrogen carrier is in reality metallic nickel freed from its compounds by the cation of hydrogen. The statement: "No hardening of fat without free metal" he believes is justified in view of the present state of the science and the exact experimentation which has been accomplished.

As a proof that the lack of electrical conductivity does not necessarily indicate the absence of metallic nickel Normann\* cites an experiment in which a contact material prepared from purified kieselguhr with about 20 per cent of nickel, reduced for an hour at 500° C. in hydrogen, showed no conductivity. On the other hand, the same kieselguhr mixed with 5 per cent of nickel, prepared by the reduction of nickel oxide at 280° C., showed pronounced conductivity.

In answer to Erdmann's assertion that the reduction of nickel oxide during hydrogenation was due to impurities in the oil, Normann describes an experiment in which 100 g. of synthetic triolein was mixed with 1 g. of pure nickel oxide and hydrogenated at 250° C. Within a few minutes a pronounced carbonyl reaction was obtained, and the mixture was strongly electrically conductive. Notwithstanding Erdmann's hypothetical assertions, Normann repeats his conclusion that without free metal there can be no hydrogenation of fats.†

By the process of Lever Bros.‡ hydrogenation is effected, while the fats employed are maintained in the liquid state, in the presence of catalyzers which are substantially suboxides of metals, especially nickel.†

The results of the studies of Erdmann and Bedford§ on the catalytic action of nickel oxides has been criticized by Meigen and Bartels (see page 128), who have made the assertion, before the Natural Science Society in Freiburg-in-Breisgau|| and later published the

\* J. S. C. I., 1916, 641; Chem. Ztg., 1916, 40, 381-383.

† J. S. C. I., 1915, 237, 969; 1916, 262.

‡ Swedish Patent No. 40,305, March 8, 1916; Chem. Abs., 1916, 1603.

§ J. prakt. Chem., 1913 (2) 87, 425.

|| Report of the Natl. Sci. Soc. in Freiburg for the session of July 17, 1913.

statement \* that nickel oxides yield bodies active as hydrogenating catalysts, only when reduction to the metallic state has taken place. Meigen and Bartels further asserted that the opinion brought forward by Erdmann and Bedford that a suboxide is formed during the reduction, is not confirmed.

In a paper of considerable length † Erdmann endeavors to disprove the conclusions of Meigen and Bartels. He first reviews the historical side of the hydrogenation prior to the work of Sabatier and Senderens. An impetus was given to the problem of oil hardening by the well-known work of Sabatier and Senderens, who recognized that finely-divided metallic nickel and several allied metals are active hydrogen conveyors. Erdmann regards the application of their method for fatty substances was natural, although not included within the range of their experiments. In 1902 the Herford Oil Works, Leprince and Siveke (page 9) applied for a German patent based on Normann's experiments, and Normann himself applied for an English patent for the conversion of unsaturated fatty acids or their glycerides into saturated compounds, employing as a catalyzer finely-divided metals, particularly nickel. According to this patent specification, Normann makes use of the process of Sabatier and Senderens of the passing of vapors over a contact metal, and also Saytzeff's process of mixing the contact substance with the liquid for the particular case of the hydrogenation of unsaturated fatty substances. Erdmann has been informed by the applicants for the German patent, that the specification was written on the strength of some test-tube experiments. The patent was granted in 1903 ‡ and such rights at least for six years existed on paper only, without being carried out on a large scale. In 1908 the Herford Oil Works operated an experimental plant for hardening fats, but abandoned it, as the process was too incomplete and the product obtained was not entirely satisfactory. In 1908 this firm sold its British and in 1910 its German patents to Crosfield & Sons in Warrington. In the factory of this English firm the catalytic process was developed, particularly by the work of Kayser. In 1911 the Dutch firm, Naamlooze Vernootschap Ant. Jurgens Vereenigde Fabrieken, acquired a license for the use of the process in Germany from Crosfield & Sons, and founded the Germania Works at Emmerich-on-the-Rhine. This plant was put into operation in 1912, 9½ years after the application for the German patent.

In German Patent No. 266,438, Erdmann claims that he and his associates were the first to ascertain that unsaturated fats may be more easily hydrogenated by the aid of finely-divided nickel oxide, than by aid of the metal. At the time of this application, that is, almost seven years after the granting of the German patent for the nickel process, fatty oils were nowhere produced on a factory scale in Germany. When Meigen and Bartels state that merely the high price of technical hydrogen was the cause of the delay in the development of the Normann process, Erdmann thinks it shows a remarkable lack of knowledge of electrochemical progress. From electrochemical factories as early even as 1902, many million cubic meters of hydrogen were allowed to escape into the air,

\* J. prakt. Chem., 1914 (2) 89, 290.

† J. prakt. Chem., 91, 469.

‡ German Patent No. 141,029; British Patent No. 1515, 1903. In 1908, according to Erdmann, Normann sold his rights in the British Patent to Leprince and Siveke for £100.

because no use was known for it. Thus, as early as 1900, Greisheim-Elektron had available in Greisheim, Bitterfeld and Rheinfelden together about 11,500 H.P. for the electrolysis of alkali chlorides. For the conditions then existing this corresponds to an annual production of 21,850 metric tons of caustic potash (or 16,100 metric tons of caustic soda) accompanied by the loss of about 4,500,000 cubic meters of hydrogen. There were soon added the great works of the Badische Co., with 8000 H.P., then the German Solvay Works, the Hoechst Dyestuff Works and various other factories. Erdmann thinks that this hydrogen would have been cheaply furnished for the hardening of oil, if the process had been technically ready.

#### EXPERIMENTAL WORK BY ERDMANN

**Hydrogenation by Means of Nickel Oxide and Metallic Nickel.** If 1 kilogram of cottonseed oil is heated to 250° C. with 5 g. of nickel oxide produced by moderate ignition of nickel nitrate, while passing a current of pure hydrogen gas at the rate of 20 to 25 liters per minute through the liquid, after one-half hour the liquid becomes black like ink. After two or three hours, if the mixture is allowed to cool, the mass solidifies to a solid in which the catalyst is suspended. For cottonseed oil, hydrogenation takes place even at 220°, for oleic acid, at 180° to 185° C.

A comparative experiment made with 5 g. of a nickel oxide, reduced by Sabatier's method at 280° to 300° C. for one hour in a current of hydrogen, with repeated agitation and the reduced material added to preheated cottonseed oil (1 kg.) on treatment with hydrogen in the same way as in the first experiment, affords no fine division of the nickel. The liquid does not become inky black, and on shutting off the current of hydrogen, the nickel powder settles rapidly. Even after passing in hydrogen for many hours, the oil does not become solid. With  $\frac{1}{2}$  per cent of nickel no hydrogenation takes place, unless the nickel is converted into finest state of subdivision possible by special methods.

Two experiments with linseed oil are noted. Nickel oxide used in both experiments, was of a voluminous character and was produced by the process of German Patent No. 260,009, of December 19, 1911, by allowing a concentrated nickel nitrate and sugar solution to drop into a glowing muffle. This catalyst is referred to as nickel oxide (vol.):

(a) Two hundred and fifty grams of the linseed oil were mixed with 1.25 g. of nickel oxide (vol.) and hydrogenated at 255° to 260° C. (b) 1.25 g. nickel oxide (vol.) were reduced for one hour at 270° C., then added to 250 g. of the linseed oil and hydrogen was passed through for several hours at 255° to 260° C.

Time in Hours.	Temperature.	SOLIDIFICATION POINT.	
		a	b
1	260° C.	Beginning of hardening, with ink-black coloration.	Sample remains light and liquid.
2	240° C.	30.7° C.	"
3	260° C.	40.3° C.	"
4	253° C.	46.5° C.	"
4	261° C.	47.2° C.	"

The conclusion that nickel oxide and not nickel is the catalyst he considers is reached from the chemical and physical examination of the recovered catalyst. This, it is true, is complicated by the fact, that it is not possible for this purpose to remove all the adhering organic substances. The recovery may be carried out by allowing the oil and catalyzer to settle for a day at 60° C. After cooling, the lower black layer of the cake is separated from the light-colored fat and is placed in a Soxhlet extraction thimble. It is then extracted for twenty hours with boiling benzol, and dried in a vacuum. The residue is placed in a fresh thimble and again extracted for twenty hours with benzol. In this way it is possible to recover a catalyst which does not contain more than a maximum of 3.5 per cent. of carbon. The coal-black powder thus obtained has reducing properties. It liberates nitric oxide from nitric acid and hydrogen from dilute sulphuric acid. It colors aqueous solutions of phosphotungstic acid and phosphomolybdic acid blue, and in this respect does not behave differently than finely-divided nickel. The degree of reduction of this substance (which is measured by the hydrogen developed), does not continuously increase with the length of time it is used as a catalyst. Erdmann has given two methods by which nickel and nickel suoxide may be differentiated, namely: by the determination of the electric conductivity and by the carbonyl reaction. By the aid of these two methods, he determined that no metallic nickel could be detected in the recovered catalyst, and that the reducing properties must, therefore, be considered as being due to a lower oxide of nickel.

For the hydrogenation experiments of the table following, cottonseed oil purified in Erdmann's laboratory, triolein found by analysis to be pure, and the purest oleic acid from Merck, were used.

## (a) COTTONSEED OIL PURIFIED BY STEAM

No.	Amount of Catalyst Gm.	Temp. ° C.	Time, Hrs.	Solidification.	Conductivity	Remarks.
1	1	210-220	3	57.2	0	No carbonyl reaction
2	5	225	1½	27.8	0	Ni = 74.3% <sup>1</sup> , H = 102 cc. <sup>2</sup>
3	8	255	4	42	0	
4	7	218	2	40	0	
5	7	235-238	3½	39.5	0	
6	5	240-243	2½	45	0	Extraction in CO <sub>2</sub> current
7	8	250-255	2½	33.5	0	
8	8	240-244	5	32.3	0	
9	8	250	1	37.7	0	Extraction in CO <sub>2</sub> current
10	8	230	1½			
11	11	239-243	3½	43.5	0	
12	11	240-245	2½	30	0	

## (b) SYNTHETIC TRIOLEIN

12	1	210-220	3	22.5	...	No carbonyl reaction
13	1	210-220	4	28	...	No carbonyl reaction
14	1	255	2½	Solid but solidification point not determined	0	Extraction in CO <sub>2</sub> current

## (c) OLEIC ACID (MERCK)

15	1	220-225	3	55.6	0	Ni = 74.4% <sup>1</sup> , H = 80.7 cc. <sup>2</sup>
16	1	200	6	57.3	0	C = 3.58% H = 0.95%
17	1	180-185	8	56	0	Ni = 76.9% <sup>1</sup> H = 81.9 cc.

<sup>1</sup> Ni content of the recovered catalyst.

<sup>2</sup> This figure relates to the amount of hydrogen (reduced to 0° C. at 760 mm.) produced from 1 g. of the recovered catalyst when treated with H<sub>2</sub>SO<sub>4</sub>.

In Nos. 1, 2, 3, 4, 5, 6, 12, 13, 14, 15, 16 and 17 voluminous nickel oxide was used. In Nos. 7, 8, 9, 10, 11, 17, 18, 19, 20, 21, 22, 23, 24, 25, 26, 27, 28, 29, 30, 31, 32, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50, 51, 52, 53, 54, 55, 56, 57, 58, 59, 60, 61, 62, 63, 64, 65, 66, 67, 68, 69, 70, 71, 72, 73, 74, 75, 76, 77, 78, 79, 80, 81, 82, 83, 84, 85, 86, 87, 88, 89, 90, 91, 92, 93, 94, 95, 96, 97, 98, 99, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116, 117, 118, 119, 120, 121, 122, 123, 124, 125, 126, 127, 128, 129, 130, 131, 132, 133, 134, 135, 136, 137, 138, 139, 140, 141, 142, 143, 144, 145, 146, 147, 148, 149, 150, 151, 152, 153, 154, 155, 156, 157, 158, 159, 160, 161, 162, 163, 164, 165, 166, 167, 168, 169, 170, 171, 172, 173, 174, 175, 176, 177, 178, 179, 180, 181, 182, 183, 184, 185, 186, 187, 188, 189, 190, 191, 192, 193, 194, 195, 196, 197, 198, 199, 200, 201, 202, 203, 204, 205, 206, 207, 208, 209, 210, 211, 212, 213, 214, 215, 216, 217, 218, 219, 220, 221, 222, 223, 224, 225, 226, 227, 228, 229, 230, 231, 232, 233, 234, 235, 236, 237, 238, 239, 240, 241, 242, 243, 244, 245, 246, 247, 248, 249, 250, 251, 252, 253, 254, 255, 256, 257, 258, 259, 260, 261, 262, 263, 264, 265, 266, 267, 268, 269, 270, 271, 272, 273, 274, 275, 276, 277, 278, 279, 280, 281, 282, 283, 284, 285, 286, 287, 288, 289, 290, 291, 292, 293, 294, 295, 296, 297, 298, 299, 300, 301, 302, 303, 304, 305, 306, 307, 308, 309, 310, 311, 312, 313, 314, 315, 316, 317, 318, 319, 320, 321, 322, 323, 324, 325, 326, 327, 328, 329, 330, 331, 332, 333, 334, 335, 336, 337, 338, 339, 340, 341, 342, 343, 344, 345, 346, 347, 348, 349, 350, 351, 352, 353, 354, 355, 356, 357, 358, 359, 360, 361, 362, 363, 364, 365, 366, 367, 368, 369, 370, 371, 372, 373, 374, 375, 376, 377, 378, 379, 380, 381, 382, 383, 384, 385, 386, 387, 388, 389, 390, 391, 392, 393, 394, 395, 396, 397, 398, 399, 400, 401, 402, 403, 404, 405, 406, 407, 408, 409, 410, 411, 412, 413, 414, 415, 416, 417, 418, 419, 420, 421, 422, 423, 424, 425, 426, 427, 428, 429, 430, 431, 432, 433, 434, 435, 436, 437, 438, 439, 440, 441, 442, 443, 444, 445, 446, 447, 448, 449, 450, 451, 452, 453, 454, 455, 456, 457, 458, 459, 460, 461, 462, 463, 464, 465, 466, 467, 468, 469, 470, 471, 472, 473, 474, 475, 476, 477, 478, 479, 480, 481, 482, 483, 484, 485, 486, 487, 488, 489, 490, 491, 492, 493, 494, 495, 496, 497, 498, 499, 500, 501, 502, 503, 504, 505, 506, 507, 508, 509, 510, 511, 512, 513, 514, 515, 516, 517, 518, 519, 520, 521, 522, 523, 524, 525, 526, 527, 528, 529, 530, 531, 532, 533, 534, 535, 536, 537, 538, 539, 540, 541, 542, 543, 544, 545, 546, 547, 548, 549, 550, 551, 552, 553, 554, 555, 556, 557, 558, 559, 560, 561, 562, 563, 564, 565, 566, 567, 568, 569, 570, 571, 572, 573, 574, 575, 576, 577, 578, 579, 580, 581, 582, 583, 584, 585, 586, 587, 588, 589, 590, 591, 592, 593, 594, 595, 596, 597, 598, 599, 600, 601, 602, 603, 604, 605, 606, 607, 608, 609, 610, 611, 612, 613, 614, 615, 616, 617, 618, 619, 620, 621, 622, 623, 624, 625, 626, 627, 628, 629, 630, 631, 632, 633, 634, 635, 636, 637, 638, 639, 640, 641, 642, 643, 644, 645, 646, 647, 648, 649, 650, 651, 652, 653, 654, 655, 656, 657, 658, 659, 660, 661, 662, 663, 664, 665, 666, 667, 668, 669, 670, 671, 672, 673, 674, 675, 676, 677, 678, 679, 680, 681, 682, 683, 684, 685, 686, 687, 688, 689, 690, 691, 692, 693, 694, 695, 696, 697, 698, 699, 700, 701, 702, 703, 704, 705, 706, 707, 708, 709, 710, 711, 712, 713, 714, 715, 716, 717, 718, 719, 720, 721, 722, 723, 724, 725, 726, 727, 728, 729, 730, 731, 732, 733, 734, 735, 736, 737, 738, 739, 740, 741, 742, 743, 744, 745, 746, 747, 748, 749, 750, 751, 752, 753, 754, 755, 756, 757, 758, 759, 760, 761, 762, 763, 764, 765, 766, 767, 768, 769, 770, 771, 772, 773, 774, 775, 776, 777, 778, 779, 780, 781, 782, 783, 784, 785, 786, 787, 788, 789, 790, 791, 792, 793, 794, 795, 796, 797, 798, 799, 800, 801, 802, 803, 804, 805, 806, 807, 808, 809, 810, 811, 812, 813, 814, 815, 816, 817, 818, 819, 820, 821, 822, 823, 824, 825, 826, 827, 828, 829, 830, 831, 832, 833, 834, 835, 836, 837, 838, 839, 840, 841, 842, 843, 844, 845, 846, 847, 848, 849, 850, 851, 852, 853, 854, 855, 856, 857, 858, 859, 860, 861, 862, 863, 864, 865, 866, 867, 868, 869, 870, 871, 872, 873, 874, 875, 876, 877, 878, 879, 880, 881, 882, 883, 884, 885, 886, 887, 888, 889, 890, 891, 892, 893, 894, 895, 896, 897, 898, 899, 900, 901, 902, 903, 904, 905, 906, 907, 908, 909, 910, 911, 912, 913, 914, 915, 916, 917, 918, 919, 920, 921, 922, 923, 924, 925, 926, 927, 928, 929, 930, 931, 932, 933, 934, 935, 936, 937, 938, 939, 940, 941, 942, 943, 944, 945, 946, 947, 948, 949, 950, 951, 952, 953, 954, 955, 956, 957, 958, 959, 960, 961, 962, 963, 964, 965, 966, 967, 968, 969, 970, 971, 972, 973, 974, 975, 976, 977, 978, 979, 980, 981, 982, 983, 984, 985, 986, 987, 988, 989, 990, 991, 992, 993, 994, 995, 996, 997, 998, 999, 1000.

## CATALYZER, ONE PER CENT OF NICKEL OXIDE (VOLUMINOUS)

No.	Oil.	Temp., ° C.	Time, Hours.	Solidifying Point, ° C.	Conductivity.	Remarks.
18	Refined cottonseed oil....	230-246	3	39	+	
19	Edible cottonseed oil....	260	1	39.2	+	
20	Pure cottonseed oil hardened to 57°	260	6	..	+	Catalyst flocculated out
21	Hardened linseed oil....	260	6	.	+	Catalyst flocculated out. H=294 cc.
22	Pure cottonseed oil hardened to 57.5° C. <sup>1</sup>	195-200	5½	..	0	No flocculation
23	Linseed oil... ..	{ 260 200	{ 1 8½	52.7	0	No flocculation
24	Oleic acid (Mcrek). .	{ 250 200	{ 1 15			
				63	0	Ni=75.2 per cent H=104 cc.

<sup>1</sup> The catalyst had already been used once and recovered.

Erdmann considers the solidification point of more significance than the iodine number, as the latter may be misleading, when polymerization has taken place. Linseed oil (Test 23) was hydrogenated for one hour at 260° C. then for 8½ hours at 200° C. After three hours the solidification point was 46.2° and did not increase with further treatment. Nevertheless the catalyst remained well divided and did not flocculate out. Nickel formation did not set in at 200° C. Oleic acid (Test 24) treated with hydrogen at 200° C. gave after nine hours a solidification point of 63°, which did not increase in several hours subsequent treatment. Nickel likewise was not formed. The conditions are favorable for formation of nickel, when a high temperature (260° C.) and a large quantity of catalyst are used with an oil such as cottonseed oil, which readily takes up hydrogen. The hydrogenation then becomes so vigorous that the temperature in the interior may be raised by the heat of reaction above that of the oil bath used for heating purposes. This spontaneous heating, it is stated, favors reduction to the metallic state. For cottonseed oil 0.5 per cent or at most 1 per cent nickel oxide (vol.) suffices perfectly for the hydrogenation.

According to Erdmann's analyses the amount of hydrogen developed by a recovered catalyst when treated with sulphuric acid never reached the amount of 233 cc. from 1 g. of substance, which would be the amount expected from a pure compound having the formula NiO. The amount of hydrogen given off is usually not even half as large as that (see tests 2, 15, 17 and 24 in the above tables) and only exceeds it when nickel was produced deliberately and was detectable by the conductivity (Test 21). Meigen and Bartels contend that they are able to refute Erdmann's statements by two analyses. (1) 0.1488 g. of catalyst produced 43.1 cc. of hydrogen (reduced to 0° at 760 mm.) and 0.1316 g. nickel (corresponding to 88.4 per cent). (2) 0.0976 g. of catalyst gave 22.6 cc. of hydrogen (reduced) and 0.0725 g. of nickel (corresponding to 74.6 per cent).

Contrary to the statements of these writers, the nickel content does not in

these analyses exceed that of the nickel suboxide,  $\text{Ni}_2\text{O}$ , as this amounts to 91.7 per cent. When Erdmann calculated these analytical results for nickel suboxide ( $\text{Ni}_2\text{O}$ ) he obtained from the first analysis the figure 140.4 per cent and in the second 134.3 per cent, which, of course, is impossible. Erdmann notes that, in some cases a part of the hydrogen generated by the action of acids may be due to the formation of hydride. Hydrided nickel oxides of the following forms are conceivable: (1)  $\text{H}-\text{Ni}(\text{OH})$ ; (2)  $\text{H}-\text{Ni}-\text{O}-\text{Ni}(\text{OH})$ ; (3)  $\text{H}-\text{Ni}-\text{O}-\text{Ni}-\text{H}$  and others. Such hydrides would necessarily produce more hydrogen with acids than a suboxide ( $\text{Ni}_2\text{O}$ ). The assumption that perhaps a mixture of such nickel oxide hydrides are present in the catalyst used for the hydrogenation is not a purely speculative one, but is corroborated by an examination of the recovered catalyst. If the latter, after drying in a current of neutral gas or in a vacuum is heated to  $250^\circ\text{C}$ . steam, in addition to small amounts of hydrogen, is found to be given off. The catalyst, thus heated, sometimes shows electric conductivity, i.e., the heating has produced nickel. In other cases, usually when the hardening has not been carried far, no nickel can be detected after the heating.

**Electric Resistance.** Tubandt, director of the physico-chemical department of the University Institute in Halle made some measurements of resistance with used nickel oxide catalysts, for Erdmann.

**Preparation of Catalysts.** (1) Linsced oil with 1 per cent of nickel oxide (vol.) was hardened for three hours. Solidification point  $42^\circ\text{C}$ . Hardening temperature  $260^\circ\text{C}$ . (one hour) and  $210^\circ\text{C}$ . (two hours). (2) Edible cottonseed oil, purified by distillation with steam, was hardened with 1 per cent of nickel oxide (vol.) for  $2\frac{1}{2}$  hours at  $250^\circ$  to  $255^\circ$  Solidification point  $44^\circ\text{C}$ .

These catalysts were pressed into tablets of 10 mm. diameter and 2 to 5 mm. height by means of a pressure of 1000 atmospheres in a steel cylinder. Platinum discs with welded platinum wires were pressed against the flat end surfaces of the tablets. In order to insure a contact with the platinum discs as free of induction resistance as possible, the ends of the tablets were gold plated. The conductivity measurements were made with a Wheatstone bridge provided with alternating current and a telephone receiver. The apparatus permitted the measurement of resistances of several millions of ohms with certainty. Tubandt made measurements of the conductivity at different temperatures from room temperature up to  $300^\circ\text{C}$ .

Catalyst (1) at  $16^\circ$  afforded a specific resistance of 3,000,000 ohms, at  $150^\circ$ , 1,600,000 ohms, at  $200^\circ$ , after heating for one hour, 376,400 ohms and after cooling to  $16^\circ$ , 300,000 ohms. After heating for two hours up to  $300^\circ$  the following measurements were taken at  $300^\circ\text{C}$ ., 196.4 ohms and after cooling to  $15^\circ\text{C}$ . 78,560 ohms. The catalyst, therefore, first shows the typical behavior of a poorly conducting metal oxide. It conducts decidedly more poorly than pure nickel oxide, for which at  $17^\circ$  a specific resistance of 10,720 ohms was determined. A difference is shown by the decrease in resistance at higher temperatures, finally reaching an almost constant point (when the temperature remains unchanged). Erdmann offers the surmise that an explanation may be found in the fact that at the higher temperature a part of the suboxide is reduced to metallic nickel by the occluded hydrogen.

Catalyst (2) at  $170^\circ$  exhibited a specific resistance of 3,000,000 ohms, and at  $61^\circ\text{C}$ . the resistance was 2,266,000 ohms. On further slow heating the resistance slowly decreases with the rising temperature. At  $270^\circ$  this decrease is very rapid. At  $290^\circ$  the resistance became 0.207 ohm and at  $16^\circ$  the figure obtained

was 9.1524 ohms. The phenomena are analogous to those observed in (1), except that on heating, so much nickel is formed that the substance becomes readily conductive. The temperature coefficient of conductivity before heating is positive—the suboxide being an electrolytic conductor of the current—and, after heating, the coefficient is negative (metallic conduction).

Erdmann concludes that all these measurements indicate the used nickel oxide catalyst not to contain metallic nickel, at least not in appreciable quantities. When nickel is actually present, either added to the catalyst at the start, or formed by the occluded hydrogen on heating the oil-free catalyst, it can be detected by measuring the electric conductivity.

Erdmann made various observations by means of the nickel carbonyl reaction to prove the presence or absence of nickel. Experiments were carried out as follows: 50 to 100 g. of the oil were heated with the addition of 1 to 2 per cent of nickel oxide (vol.) in a flask (only vessels of glass can be used), with bottom tube, and the oil hydrogenated to a solidification point of 28° to 33° C. The glass flask was then heated in a water-bath at 30° to 35° C. Hydrogen was replaced by pure dry carbon monoxide which was led into the flask by means of a T tube from a gasometer. Thus, there was no necessity of transferring and exposing hardened fat during the test. For a period of fifteen to thirty minutes no nickel mirror was formed on heating the escaping gas passing through a glass tube used for the mirror test. A colloidal solution of metallic nickel in oil, obtained by electric atomizing of reduced nickel into linseed oil, was tested in the same way; 50 cc. of the colloidal solution, whose nickel content was 0.046 g., were placed in the flask. A nickel mirror was at once obtained. A nickel mirror was obtained within three minutes when carbon monoxide was passed over dry metallic nickel at 34° C. which had been obtained by reducing 0.13 g. nickel oxide (vol.) with hydrogen.

By these tests, Erdmann considers it is proven, even when only small amounts of nickel are present, that a temperature of about 30° C. is actually sufficient for the formation of the nickel carbonyl. If at 30° C. during the course of fifteen minutes no mirror is produced by carbon monoxide, Erdmann states this proves the absence of metallic nickel.

The following experiments also were made:

One hundred cc. cottonseed oil were hardened with the addition of 1 g. nickel oxide (vol.) for  $\frac{1}{2}$  hour at 250° to 255° C. The ink-like liquid was then treated at 50° with dry carbon monoxide in the same flask. The escaping gas flowed through a heated glass tube and then was ignited. In the first ten minutes no mirror was formed, nor were any dark spots formed on a piece of porcelain when held over the flame. After seventeen minutes such spots were formed and a nickel mirror appeared. After thirty minutes the mirror was heavy, the carbon monoxide flame had an internal cone with a luminous point and readily deposited nickel spots on porcelain. The experiment was repeated at 60°, at 70° to 75° and at 80° to 85°. Highly hardened cottonseed oil was also used, but without producing any change in the result. A certain period of time always elapses before a deposition of nickel becomes noticeable. However, it is easy to overestimate the amounts of nickel deposited. The weight of the heavy-appearing nickel mirror deposited during half an hour at 50° in the above experiment amounted only to a few tenths of a milligram. A second experiment at 70° to 75° for a full hour furnished a nickel mirror of 2.2 milligrams and a third at 80° to 85° for one hour a mirror weighing 2.7 milligrams.



The dependence of the reaction on the temperature, and its almost negative result at 30° point to a reducing action by the carbon monoxide.

By a determination of the amount of carbon dioxide formed, it is proven that at 80° to 85° C. carbon monoxide has a reducing action on the nickel compounds contained in the hardened fat.

A thesis by Agde \* considers the subject of nickel oxide as a catalyzer, from a number of aspects. In order to study the question whether, and under what conditions metallic nickel is formed during the hydrogenation of fatty substances in the presence of nickel oxides, it appeared necessary to use as raw material for the experiments, chemically pure substances, or at least natural fatty oils purified as far as possible. Only under such conditions is it possible to exclude secondary reactions. Agde has therefore mainly used chemically pure oleic acid, synthetic triolein and a cottonseed oil carefully freed of aldehydes.

If voluminous nickel oxide prepared from nickel nitrate, as used by Agde in most of the experiments, is introduced into the hot oil and hydrogen passed through in a vigorous current, then the grey color of the catalyst is changed to yellow-green. It then spreads through the oil, more or less rapidly, depending on the temperature, colors the oil grey and finally black. This last change of color into grey to black is an indication of the commencement of the hardening of the oil. With the glycerides this distribution takes place more rapidly and completely than with the free fatty acid. Agde has also determined that with the glycerides colloidal transfusion or distribution occurs. When the black liquid is treated with benzol, then filtered through hardened filter paper, clear deep brown filtrates were obtained which were examined under the ultramicroscope. The filtrate from synthetic triolein showed mainly amicroons and that from cottonseed oil only submicroons.

A nickel oxide catalyst used for a second time, distributes in the oil at once, thereby shortening the time for the hardening. The catalyst cannot be used as often with oleic acid as with a glyceride. The frequency of this re-use naturally also depends upon the original amount of the catalyst. With 2 per cent of catalytic substance successive portions of oleic acid could be highly hardened three times. With 1 percent of catalytic substance the nickel oxide was flocculated out when used a third time—a sign that its activity was ceasing and with  $\frac{1}{2}$  per cent of catalyzer this flocculation took place during the second hardening of the oleic acid.

The required initial temperature varies for different oils. For oleic acid it is comparatively low, Agde determined it as being 180° to 185° C. But at such a low temperature the hardening takes place slowly. Over seven hours duration were necessary to reach a solidification point of 56°, while the same result was obtained in three hours at 225° C. This is in part caused by the fact that the first phase, the distribution stage, requires a long time. The course of the hardening of oleic acid was ascertained for the temperatures from 180° to 250° C. For glycerides, such as triolein, cottonseed oil and linseed oil, the initial temperature

\* Halle, 1914, under Dr. Erdmann.

lies beyond 200° C. (for triolein at 210° to 220° C.) But when once the hydrogenation has started the temperature can be lowered for its further progress. Agde, therefore, differentiates between initial temperature and hardening temperature. Oleic acid hardening takes place at 100° to 110° if it has once been started.

The hardening curves up to a certain degree rise sharply and then curve more gradually. The commencement of the gradual curvature is dependent on the hardening temperature and the amount of the catalytic substance. With a hardening temperature of 250° and 1 per cent of catalytic substance this curvature is found at the solidification point 61° for oleic acid; for triolein it is at about 45°.

The formation of nickel aside from being produced by the aldehydic impurities already mentioned according to Agde can be occasioned only by *overhardening*. It is favored by a high hardening temperature. Although the catalyst was still free of nickel, after hardening oleic acid for 4½ hours at 250° C. to solidification point of 63° the metal was formed after hardening for 6½ hours at 255° to a solidification point of 64°. Oleic acid could, however, be hardened at 200° and treated for fifteen hours with a strong current of hydrogen (5 liters per minute) without it being possible to detect metallic nickel in the catalyst.

In general, Agde states, with faulty carrying out of the hardening operation or with poor catalysts, oleic acid will give occasion for the formation of metallic nickel more readily than is the case with the glycerides. This is shown by an experiment in which basic nickel carbonate was added to free oleic acid at ordinary temperature, whereupon it was warmed very slowly. Under these conditions nickel oleate is formed, which sets nickel free at a high temperature under the influence of hydrogen. The catalytic action is thereby destroyed; for the nickel which is produced in this way is in the form of metallic scales and according to Agde has as little power to transfer hydrogen as has the reduced nickel formed by over hardening the oil.

Preparations of nickel oxide, which—on account of the admixed impurities which they contain (for instance, too high an alkali content), do not transfuse or distribute in the oleic acid—may also be reduced to nickel accompanied by a loss of their catalytic activity. In the apparatus used, a flask with bottom inlet tube, this is favored by the fact that the nickel oxide is precipitated as a heavy deposit in the bottom tube, while the oil is forced out of the tube by the strong current of hydrogen, thus the nickel oxide is heated directly in a hydrogen atmosphere.

The criticism that metallic nickel loses its conductivity by being acted on by the oxygen of the air during the recovery of the catalyst is also refuted by Agde, who filtered and extracted the catalyst in a current of carbon dioxide, but the results were the same as those from the experiments made without the use of this gaseous atmosphere. The test for the presence of metallic nickel by means of carbon monoxide is also negative for normal hardening. But the temperature during the action of the carbon monoxide must not be too high, as otherwise nickel oxide, it is stated, is also reduced by it and converted into nickel tetracarbonyl.

In a number of cases Agde made a quantitative analysis of the used nickel oxide catalyst which had been carefully decreased by means of benzol. It may be noted here that the nickel content lay between 75.2 per cent and 77.1 per cent, the carbon content between 2.9 per cent and 6.2 per cent and the hydrogen content between 0.7 and 1.3 per cent. The amount of hydrogen produced by

acids varied between 80.7 and 108.6 cc., calculated for 1 g. of catalyst, while 1 g. of a nickel suboxide,  $\text{Ni}_2\text{O}_3$ , theoretically yields 167.9 cc. of hydrogen (1 g. of  $\text{Ni}_2\text{O}_3$  can furnish 233.1 cc. of hydrogen). When the recovered catalyst has been used for hardening for a long time and at a high temperature, it develops foul-smelling gases when mineral acids are poured over it. These gases have an odor which remind one of the odor produced when iron carbides are dissolved in mineral acids. If the hardening be carried out at low temperatures, or if it is of short duration, this odor cannot be perceived. Furthermore the observation was made that the recovered catalyst on being heated over  $200^\circ\text{C}$ . develops hydrogen and at  $250^\circ$  to  $275^\circ\text{C}$ . splits off water. In addition small amounts of carbon monoxide were also set free. This development of gas and steam also takes place when a perfectly anhydrous nickel oxide and a carefully dried oil had been used for the hardening.

The final product of the hardening of oleic acid is a stearic acid having a melting-point of  $63^\circ$  which corresponds to an iodine number of 15.6. With triolein, however, an iodine number approximately zero is attained. The saponification number in this case agrees with that for pure tristearin and the acid number is zero. Therefore, during the hardening, nickel oxide does not produce any saponification.

Agde performed some experiments with several other organic bodies, in addition to oleic acid and fatty oils, in order to determine how nickel oxide suspended in these substances behaves when heated during the passing through of hydrogen. With paraffin and diphenylamine there resulted a rapid reduction to metallic nickel. In paraffin the nickel is already detectable after one-quarter of an hour, and after one hour the nickel content of the recovered catalyst amounts to 94.9 per cent. In the presence of beta-naphthol, acetanilid, anthracene or phenanthrene, however, there is also a reduction of the nickel oxide but after from one to four hours treatment with hydrogen at  $250^\circ$  it is not reduced to the metallic state. Evidently the last-named substances exert a protecting influence on the metallic oxide. No connection between the division or distribution of the nickel oxide and the viscosity of the substances could be proven.

Agde considers his studies to have proven beyond all doubt that in the oil-hardening process of Bedford and Erdmann, metallic nickel is not the conveyor of hydrogen. He claims that easily avoidable errors have been discovered which explain the chance formation of nickel and which undoubtedly caused such a formation in the experiments of Meigen and Bartels. The determination that the nickel produced by a reduction process in the oil, is not capable of acting as a catalytic hydrogen conveyor, Agde believes furnishes ample confirmation of this view.

Concerning the mechanics of the catalytic activity of nickel oxide, it may be noted that Ipatiew has already advanced the idea, and Bedford and Erdmann have brought forth experimental indications that some lower oxide of nickel is the actual conveyor of hydrogen. But this does not exclude the possibility that perhaps nickel oxide ( $\text{NiO}$ ) is also capable of taking up and transferring hydrogen without being reduced.

Senderens and Aboulenc\* assume the formation of a nickel suboxide during the reduction of nickel oxyhydrates below  $300^\circ\text{C}$ . Such an intermediate phase is also indicated by the results of work by Sabatier and Espil† on the reduction of nickel oxide in a current of hydrogen at different temperatures. For instance,

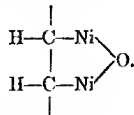
\* *Z. angew. Chem.*, 1913, 26, 209.

† *Comp. rend.*, 1914, 158, 668.

when 75 per cent to 79 per cent of the oxygen which is combined with the nickel, is converted at 200° C. into water, the curve of the velocity of reduction assumes an entirely different direction, as the speed drops greatly. This is a sure sign, Agde states, that an intermediate product, i.e., a lower nickel oxide, has been formed which is reduced much more slowly than the initial oxide. For the suboxide formed by the reduction in a current of hydrogen, Sabatier assumes the formula  $\text{Ni}_2\text{O}$ , but the way in which he calculates this formula is not very convincing to Agde. In doing this he appears to neglect the fact, that during the first phase, the sharp ascent of the curve, nickel suboxide is also further reduced to nickel, and also he does not take into consideration the fact that the speed of reaction is a function of the surface. In Agde's opinion the formula,  $\text{Ni}_2\text{O}$ , of Sabatier has no value other than to show that during the reduction of nickel oxide in a current of hydrogen at temperatures of 180°, 200° C. and higher, a nickel suboxide is produced as an intermediate phase.

Agde observes that the conditions for the reduction of the nickel oxide suspended in oil are materially different than those occurring during the reduction in a dry atmosphere of hydrogen. If, as Sabatier observed, small amounts of water considerably slow down the reduction of nickel oxygen compounds, Agde thinks it is safe to assume that large amounts of fatty oils will possess such a delaying action to a still higher degree. At all events, he continues, an explanation of the fact that, as proven, no nickel is produced during the hardening of the oil, but that the reduction here ceases at an intermediate phase as a nickel suboxide, is furnished by Erdmann\* in a most plausible way by his assumption of an addition compound of the nickel oxide with unsaturated fatty substance. By such assumption that the nickel suboxide first formed enters a complex compound by addition and is shielded from any further reduction by hydrogen an explanation is afforded of the results noted. Examples of this kind are to be found in other fields. For instance, palladium chloride is not precipitated from an acetone solution by the introduction of hydrogen as it combines with the ketone to form a double compound, while palladium solutions which do not contain such a double compound are rapidly reduced to the metallic state by hydrogen. That atoms of a metal may add themselves directly to carbon is proven by many examples in organic chemistry, such as zinc-methyl, the organo-magnesium compounds of Grignard, nickel tetracarbonyl, acetylene copper and acetylene-silver. Reference also should be made to the work of Fokin † on the addition of metallic oxides or of metallic hydroxides to form double-compounds. This experimenter has shown that during the hydrogenation of glycerides, complex compounds of platinous hydroxide with unsaturated fats are produced in the form of sols.

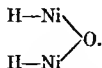
The phenomena which take place during the hydrogenation of unsaturated fatty substances with nickel oxide Agde asserts are to be considered in an analogous way. The constitution of this hypothetical addition compound of nickel suboxide can be pictured in the following way:



\* Oester. Chem. Ztg., 16, 293, Abstract.

† J. Russian Phys. Chem. Soc., 1910, 42, 1075, also 1912, 44, 653. (See Chem. Ztg., 1913, 37, 61, and Chem. Centr., 1910, Part 2, 1743.

In the further progress of the hydrogenation, the addition compound, having become charged with hydrogen supposedly is then split up into the saturated fatty substance and a nickel suboxide containing hydrogen, to which may be ascribed the formula:



When the hydrogenation has progressed so far that only a small amount of unsaturated compound still remains, then if the temperature is high enough, the nickel suboxide is further reduced to metallic nickel as is also the case if nickel oxide is treated with hydrogen in the presence of stearic acid or paraffin at 250° C. But the presence of the fatty acid advances the reduction temperature of nickel suboxide so high that the formation of nickel at 200° C. does not take place even after treating with hydrogen for fifteen hours.

Certain aromatic substances, such as acetanilide, cinnamic acid,  $\beta$ -naphthol, anthracene, and phenanthrene, have, as Adge was able to determine, the property of protecting the nickel oxide from being reduced down to the metal, without taking up hydrogen themselves at ordinary pressure.

Regarding the more or less fine division of the catalyst the following may be noted: An exceedingly fine division of the catalyst takes place in connection with the reduction of the nickel oxides in unsaturated fats, but for various substances varying degrees of fineness are observed. As already mentioned, with the glycerides, the degree of subdivision is actually colloidal, but not with oleic acid and the other organic compounds used for the experiments. The original supposition of Adge that the degree of division might stand in relation with the viscosity of this substance has not been corroborated, for linseed oil and glycerine have the same degree of viscosity and the state of division is colloidal in the former, but not in the latter, Adge has, therefore, accepted the assumption of Bedford and Erdmann that this division is related to the unsaturated condition. Presumably, Adge states, there is formed an addition-compound of an unsaturated organic body and the lower nickel oxide, which has the property of existing in the colloidal condition. The purer the oils, the more easily is a colloidal division obtained, but in this connection the temperature and the length of hardening also have some influence.

The hypothesis of the formation of an addition compound serves in the first place as an explanation of the stability of the nickel suboxide toward hydrogen. But other reasons also bespeak the entrance of the nickel oxide into organic combination. Bedford and Erdmann have already called attention to the fact that it is impossible to entirely free a catalyst, used for fat hardening, of its content of organic substance, by extracting with benzol, similar to the way in which Wieland\* treated palladium black. However, Adge found that the nickel oxide treated with hydrogen in molten paraffin or diphenylamine could be obtained absolutely free of carbon after extraction with benzol.

The appearance of a nickel carbide-like substance Adge believes also points with certainty to a compound of nickel with carbon. Furthermore, the fact that during the hardening no saponification of the triolein is brought about by

\* Ber., 1912, 45, 488.

the nickel oxide leads to the assumption of the formation of an addition-compound.\*

The fact that the hydrogenation cannot be completed with oleic acid, indicates that a condition of equilibrium takes place here, between oleic acid, its addition-compound and stearic acid. This condition of equilibrium is constant at 200° C. but at 250° with continued introduction of hydrogen, is displaced and the nickel suboxide set free is then further reduced to nickel.

Another communication by Normann† on the hydrogenation of fats in the presence of metallic nickel and nickel oxide refers to the findings of Erdmann that the hydrogenation of fats is effected more rapidly in the presence of unreduced nickel oxide than with catalyzers of nickel reduced from such oxide, whereas Normann's experiments give different results, nickel oxide material being rendered active only after reduction to the metal.

Normann observes that comparative experiments with different nickel oxides and with the metal reduced from them have shown that the activity varies with the physical form of the metal. In the case of some forms no hydrogenation could be brought about. In all cases Normann observes the metal was superior to the oxides. For instance he notes that certain impurities in commercial oxides have an unfavorable effect upon the metal reduced therefrom. He found that a small amount of hydrochloric acid had no effect on the oxide but produced a stimulating effect on the metal. Salt behaved in an analogous manner. Sulphuric acid, he claims, promotes the activity of both oxide and metal catalysts when present in small amount. He also mentions a fact long known to oil-hardening chemists that the hydrogenation of oils may be carried out technically by means of metallic nickel without any carrier.

A series of comparative tests have been carried out by Siegmund and Suida‡ on the relative value of nickel and nickel oxide in hydrogenating oils with hydrogen at atmospheric pressure.

The oils used were:

- A. Linseed oil, iodine number 176.2, acid number 6.07.
- B. Linseed oil, iodine number 170.5, acid number 3.58.
- C. Cotton oil treated six hours in vacuo at 150° to 160° C. with steam to remove aldehydes, dried for two hours in vacuo at 140° to 150° C. in contact with hydrogen. Iodine number 99.2, acid number 0.32.
- D. Cotton oil, iodine number 105.8, acid number 0.89.
- E. Rape oil, iodine number 101.9, acid number 6.61.
- F. Sesame oil, iodine number 102.3, acid number 3.44.

\* Metal oxides free of water are observed always to have a saponifying action on fats at 250. C. (For literature see Hefter. *Technologie der Fette und Oele*, 1910, Vol. III, 523.) Furthermore by the reduction of NiO to suboxide, some water is formed.

† Chem. Ztg., 40, 757; J. S. C. I., 35, 1070; Chem. Abs., 1917, 1321.

‡ J. Prakt. Chemie, 1915, 442.

The following catalytic materials were employed:

(a) Voluminous nickel oxide prepared according to Bedford and Erdmann by dropping small portions of a solution of nickel nitrate and sugar on a surface heated to a low red. The product contained carbon, 0.42 per cent, hydrogen, 0.66 per cent, and nickel, 76.67 per cent. The calculated content of nickel in nickel oxide,  $\text{NiO}$  is 78.57 per cent.

(b) Metallic nickel, obtained by reduction of voluminous nickel oxide in hydrogen at  $280^\circ$  to  $290^\circ \text{C}$ .

(c) Basic nickel carbonate (Kahlbaum).

(d) Nickel formate, prepared by dissolving nickel oxide, or better, basic nickel carbonate in warm formic acid, evaporating the solution and repeatedly crystallizing from a weak solution of formic acid. The crystals were dried over sulphuric acid. The product corresponded to the formula  $\text{Ni}(\text{HCO}_2)_2 + 2\text{H}_2\text{O}$ .

#### THE HYDROGENATING PROCEDURE

The oil was placed in a glass flask (Bedford and Erdmann type) and heated in an oil bath to  $120^\circ$  to  $180^\circ \text{C}$ . while a slow stream of hydrogen was passed through. The catalyzer was then added and the hydrogen current increased to 15 to 20 liters per minute, while the temperature was raised to  $230^\circ$  to  $260^\circ \text{C}$ . and was maintained at this point during the entire hydrogenation stage. After hardening, the fat was filtered from the catalyzer in an atmosphere of carbon dioxide. Fuller's earth was added and a second filtration made to render the fat free of catalyzer.

#### NICKEL OXIDE AS A CATALYZER.

250 g. of linseed oil, A and B, were used in each of the following tests.

Test No.	Iodine No. of Oil Used.	Amt. of Catalyzer in Gms.	Hardening Temperature	Liters of Hydrogen per Minute	Period of Hardening. Hours.	Iodine No. of Product.
XX	170.5	2.5	$250-260^\circ \text{C}$ .	18	$\frac{1}{2}$	144
XX	170.5	2.5	$250-260^\circ \text{C}$ .	18	1	111
XX	170.5	2.5	$250-260^\circ \text{C}$ .	18	$1\frac{1}{2}$	86.6
XX	170.5	2.5	$250-260^\circ \text{C}$ .	18	2	62.4
XX	170.5	2.5	$250-260^\circ \text{C}$ .	18	3	19.8
I	176.2	2.5	$240-260^\circ \text{C}$ .	18	$3\frac{1}{2}$	5.34*
VI	176.2	5.0	$273-258^\circ \text{C}$ .	10	19	1.05
450 g. cotton oil D were used in the following						
VIII	105.8	4.5	$237^\circ$	20	1	45.75
IX	105.8	4.5	$239-243^\circ$	20	2	16.8
X	105.8	4.5	$244^\circ$	20	3	5.03

\* Solidified at  $35.2^\circ$  after two hours;  $42.5^\circ$  after  $2\frac{1}{2}$  hours, and  $47.4^\circ$  after  $3\frac{1}{2}$  hours.

## HARDENING OF LINSEED OIL WITH BASIC NICKEL CARBONATE.

500 g. Oil A. 10 g. Catalyzer.

Temp.	Time.	Iodine No.
232° C.	1 hour	66.9
232-252	2 hours	45.3
233-265	3 hours	37.3
245-256	4½ hours	25.5

## HARDENING OF SESAME OIL WITH BASIC NICKEL CARBONATE.

450 g. Oil. 6.8 g. Catalyzer. Temperature 241°-248° C.

Time.	Iodine No.	Solidification Point.
½	73.3	18°
1	65.2	25.6
1½	58.0	31.6
2	54.5	34.8
2½	50.3	37.7
3	43.8	39.8

## COTTONSEED OIL C AND D, RAPESEED OIL E USING BASIC NICKEL CARBONATE

Amount of Oil.	Kind.	Amount of Catalyzer.	Temp.	Time.	Iodine No.
150	C	3	237-258° C.	2½ hours	68.7
280	D	4.2	248° C.	6 hours	26.3
450	E	6.8	248-250° C.	2 hours	58.5

## LINSEED OIL B, USING A MIXTURE OF METALLIC NICKEL AND NICKEL CARBONATE

0.15 g. reduced NiO with 5.88 g. Nickel Carbonate.

Temp.	Time.	Iodine No.
235-243° C.	1 hour	38.15
240-250° C.	3 hours	8.4

300 g. oil used in each case.

## LINSEED OIL B, WITH NICKEL FORMATE.

Temp.	Amount of Nickel Formate.	Time.	Iodine No.
243°-257° C.	8 g.	2 hours	24.7
208°-216° C.	8 g.	3 hours	3.5

300 g. oil used in each case.



## LINSEED OIL A, WITH METALLIC NICKEL AS CATALYZER.

250 g. Oil, 2.5 g. Catalyzer, Temperature 242-252° C.

Time. Hours.	Iodine No.
$\frac{1}{2}$	155.7
1	147.4
$1\frac{1}{2}$	140.9
2	134.5
$2\frac{1}{2}$	126.9
3	120.4

If the values found for linseed oil are charted, the following curves are obtained, Fig. 47d.

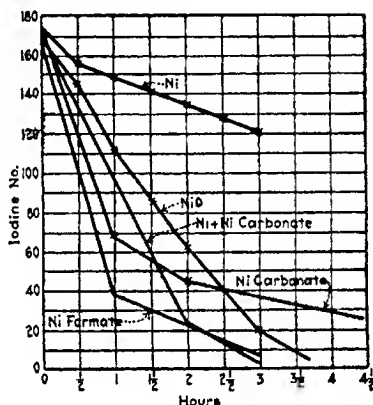


FIG. 47d.

From the curves Siegmund and Suida conclude that the speed of reaction, other things being equal, is greater for the whole reaction period for nickel oxide than for nickel carbonate. For the latter it is only very great at the beginning and it is smallest for metallic nickel. The mixture of metallic nickel with nickel carbonate at first has the greatest speed of reaction but this is later surpassed by that of nickel formate. Meigen and Bartels \* state: "If water plays any role then the speed of reaction when using nickel oxide (as already emphasized by Ipatiew) must be initially greater than with nickel, as a larger amount of water can be formed from the oxide. Ipatiew believes that he has found corroboration of this in his experiments." The above experiments are claimed to be a new proof of the correctness of this view. The latter explains at once why the initial speed is greater when utilizing basic nickel carbonate or basic nickel formate as catalysts than with nickel oxide. That nickel and nickel carbonate and particularly nickel formate have a somewhat greater reduction catalytic action than nickel oxide may be sought for, on the one

\* J. prakt. Chem. (2) 89, 292, 1914.

hand in their greater initial speed of reaction, and on the other hand, that with them an oxide poorer in oxygen (nickel suboxide) is more readily formed.

From the analyses of the used and purified catalysts it appears that all contain organic substances in a form insoluble in benzol, in greater or lesser amounts. If we take into consideration the fact that all the oils used for the experiments contain free fatty acids, the conclusion is probably justified that the organic substance contained in the used and purified catalysts is a nickel salt of a fatty acid. (According to actual experiments nickel oleate is soluble and nickel stearate insoluble in benzol). All used catalysts were attracted more or less by magnets with the usual characteristic brush formation.

Experiments made by Siegmund and Suida gave evidence that on heating nickel carbonate at 250° C. in a current of hydrogen in oils almost entirely free of acid, large amounts of carbon dioxide escape. On using oils not free of acid, there will first be a formation of nickel soap with evolution of carbon dioxide.

Nickel formate, was gradually heated up to 250° C. in a current of nitrogen in a metal bath. Duration of the heating, one hour. The escaping gases were led over glowing CuO and then through a CaCl<sub>2</sub> tube and a potash bulb.

Calculated for Ni(HCO <sub>2</sub> ) <sub>2</sub> + 2H <sub>2</sub> O	Found
CO <sub>2</sub> 47.37 per cent (=12.92 per cent C)	47.23 per cent (=12.88 per cent C)
H <sub>2</sub> O 29.16 per cent (= 3.12 per cent H)	28.10 per cent (= 3.12 per cent H)
Residue 33.83 per cent.	

Nickel formate was heated gradually as above up to 250° C. for 1½ hours in a current of nitrogen in a metal bath. The escaping gases were freed of water and CO<sub>2</sub> direct in the CaCl<sub>2</sub> tube and potash bulb without previous passing over CuO.

Calculated for Ni(HCO <sub>2</sub> ) <sub>2</sub> + 2H <sub>2</sub> O	Found
CO <sub>2</sub> 47.37 per cent (=12.92 per cent C)	42.30 per cent (=11.54 per cent C)
H <sub>2</sub> O 29.16 per cent (= 3.23 per cent H)	18.62 per cent (= 2.07 per cent H)
Residue 34.27 per cent.	

Accordingly by simple heating to 250° C. nickel formate is decomposed into CO<sub>2</sub>, CO, H<sub>2</sub>O and hydrogen and there remains a product which in addition to 31.51 per cent of nickel, in the main contains oxygen also.

This residue is dark grey-black in color and is magnetic. Its specific gravity is 5.788 at 20° C., its conductivity is zero. The composition is approximately Ni<sub>3</sub>O and the carbonyl test gave no evidence of metallic nickel. In order to ascertain the behavior of nickel formate at a somewhat lower temperature, it was heated for 1½ hours in a current of nitrogen to 200° C. In this time the absorbing apparatus took up 9.62 per cent CO, and 11.17 per cent H<sub>2</sub>O, showing that nickel formate begins to decompose at temperatures under 200° C.

The conclusions of Siegmund and Suida are that: 1. Under ordinary pressure the hardening of fat takes place incomparably more rapidly with nickel oxide than with metallic nickel. 2. When using nickel carbonate and nickel formate as catalysts the hardening of fat proceeds exactly in the same way as when nickel oxide is used. 3. The used catalysts obtained when nickel oxide, nickel carbonate, nickel formate and metallic nickel + nickel carbonate are used have approxi-

mately the same composition. 4. The hardening of fat with nickel carbonate, nickel formate, or a mixture of nickel+nickel carbonate is identical with the hardening when using nickel oxide. In this hardening a low oxide of nickel is the conveyor of the hydrogen. This hardening is materially different from that made with metallic nickel. 5. In those hydrogenation processes in which a low nickel oxide is the hydrogen conveyor, water plays a role.

## CHAPTER IX

### NICKEL CARBONYL

Owing to the interest manifested in nickel carbonyl as a source of catalytic nickel and because of the difficulties encountered in its preparation the following extracts from various publications on the subject are appended.

The action of carbon monoxide on nickel was noted by **Mond** and associates in 1890.\* When carbon monoxide is passed over finely-divided nickel, such as is obtained by reducing nickel oxide by hydrogen at about 400 degrees, at a temperature between 350 and 450 degrees, carbon dioxide is formed, and the nickel is gradually converted into a black, amorphous powder, consisting of carbon and nickel; the composition of this deposit varies widely with temperature and time. A small quantity of nickel can thus change a very large amount of carbon monoxide, the action being complete and rapid at first, and continuing, although at a diminishing rate, for several weeks. A product containing as much as 85 parts carbon to 15 parts nickel was obtained. Acids only partially remove the nickel; the carbon is very readily acted on by steam, carbon dioxide and hydrogen without a trace of carbon monoxide being formed at a temperature of 350 degrees.

On allowing the substance to cool in a current of carbon monoxide, it was noticed that the flame of a Bunsen burner into which the escaping gas was introduced became luminous, and when the tube through which the gas passed was heated, a deposit of nickel, mixed with a small quantity of carbon, was obtained. Mond and his associates were thus led to discover the existence of a volatile nickel compound.

To prepare this compound a combustion tube was filled with nickel oxide and this was reduced by hydrogen at about 400 degrees; after cooling the nickel to about 100 degrees, pure dry carbon monoxide was passed over it without further heating, and the issuing gas led through a tube placed in a freezing mixture; the major portion of the nickel compound condensed as a colorless liquid; but since the gas retained about 5 per cent, it was collected, dried and again passed over the metal. When no more liquid condensed, the nickel was again

\* Mond, Langer and Quineke, *Proc. Chem. Soc.* (1890), 112; *J. S. C. I.* (1890), 808.

heated to about 400 degrees in a slow current of pure carbon monoxide; it was then cooled to about 100 degrees, and again submitted to the action of the gas.

Nickel carbonyl thus prepared is a colorless liquid, which boils at 43 degrees under 751 mm. pressure; its relative density at 17 degrees is 1.3183. It solidifies at -25 degrees to a mass of needle-shaped crystals. Its composition is represented by the formula  $\text{Ni}(\text{CO})_4$ . It dissolves in alcohol, and more readily in benzene and chloroform; dilute acids and alkalis have no action on it, but it is oxidized by concentrated nitric acid. It reduces an ammoniacal solution of cupric chloride, and also causes the separation of silver from an ammoniacal solution of silver chloride. It interacts with chlorine, forming nickel chloride and carbon oxychloride. It is decomposed at 180 degrees (in boiling aniline vapor) into nickel and carbon monoxide. The atomic weight of the deposited metal was found in three experiments to be 58.52 to 58.64, a result closely corresponding with Russell's value, 58.74.

Numerous experiments to obtain similar compounds with other metals, notably with cobalt, iron, copper and platinum, led to negative results. On experimenting with specially-purified cobalt, in the beginning a slight coloration of the Bunsen flame into which the gas was led was noticed, but after a time this was no longer observed. Commercial cobalt afforded a gas which deposited a mirror of pure nickel, it being possible, in fact, to purify cobalt from nickel by carbonic oxide. The nickel mirrors obtained by heating the carbonic oxide compound do not appear to contain any trace of cobalt.

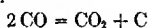
Martha (Chem. Ztg. (1891), 915; J. S. C. I., 1891, 837) has recorded some properties of nickel carbonyl which are of interest. He used some impure ferriferous nickel oxide as the source of the metal. Under these circumstances the condensed nickel compound has always a yellow tinge, and contains iron, as do also the nickel films obtained by heating the conducting tube. The liquid after standing for a few hours, even in a sealed tube, deposits a brown compound containing iron, which often explodes with great violence when the liquid is poured off, the sides of the tube being simultaneously covered with a film of nickel. An apple green precipitate containing nickel is occasionally deposited, together with the brown iron compound, and adheres strongly to the sides of the tube. The vapor of the liquid compound exploded upon one occasion very violently, either owing to the presence of a particle of the iron compound or to its own explosive properties.

Berthelot \* notes that the vapor tension of nickel carbonyl (boiling point 46° C.) at 16° C. is about one-fourth of an atmosphere. A drop of the liquid allowed to evaporate spontaneously forms a certain quantity of crystals, which consist of the solidified substance, and speedily volatilize on continued exposure. It has no sensible tension of dissociation at the ordinary temperature, but in contact with air

\* Bull. Soc. Chim. (1892), 13, 431.

oxidizes rapidly. The precise mechanism of oxidation varies according to the conditions under which it takes place. For example, when an inert gas, charged with the vapor of nickel carbonyl, is passed through a strongly heated tube, the products are metallic nickel and carbon monoxide, as observed by Mond and his colleagues. These investigators also found when nickel carbonyl is heated sharply to 70° C., at which point detonation takes place, that the same bodies are formed.

Berthelot, however, has observed that a certain amount of carbon dioxide and carbon is produced. He is of the opinion that this reaction determines the occurrence of the detonation, as the equation



implies the evolution of 38.8 calories, i.e., 77.6 calories for the 4 mols. of carbon monoxide in  $\text{Ni}(\text{CO})_4$ . The only assumption necessary to justify this view is that the heat of combination of Ni and CO is less than 77.6 calories.

The reactions of nickel carbonyl are generally those dependent upon the presence in it of nickel, but when they are induced gently and at low temperature, bodies comparable to organo-metallic compounds are formed. The vapor of nickel carbonyl is not sensibly soluble in water or dilute acid or alkaline solutions or cuprous chloride. Hydrocarbons are its natural solvents; spirits of turpentine is specially suitable, and can be used for determining it. Explosion of a mixture of nickel carbonyl and oxygen can be effected by violent agitation over mercury as well as by direct ignition. Slow union takes place when such a mixture is kept in contact with a little water. In contact with strong sulfuric acid dry liquid nickel carbonyl explodes after a short interval, but if in the form of vapor and diluted with nitrogen it is decomposed gradually, the theoretical quantity of carbon monoxide being liberated. Strong caustic potash has no perceptible action on nickel carbonyl. Gaseous ammonia does not act immediately per se, but if a little oxygen be added, fumes are produced, and if the action of oxygen be continued a whitish deposit of complex composition is gradually formed which is destroyed with charring on being heated.

Sulfuretted hydrogen acts on nickel carbonyl vapor, mixed with nitrogen in the cold, a black sulfide (of nickel) being precipitated. Phosphoretted hydrogen under similar conditions gives a brilliant black deposit. Nitric oxide if mixed with nickel carbonyl vapor, diluted with nitrogen, or passed into the liquid itself, produces blue fumes, which fill the whole vessel. The formation of nickel carbonyl proves carbon monoxide to be capable of forming organo-metallic compounds similar to those derived from hydrocarbons, and analogous to the salts of rhodizonic and croconic acids produced by the union of

the condensed derivatives of carbon monoxide with an alkaline metal. Nickel carbonyl serves as an example of the tendency of carbon monoxide to form loose combinations and products of condensation, in virtue of its character as an unsaturated body.

Nickel carbonyl, according to Berthelot,\* can be preserved under water, but if contained in a bottle with an ordinary ground-in stopper becomes slowly oxidized, and a layer of apple green nickel hydrate is formed, which is free from carbon. A portion of it, however, makes its way out of the bottle and is oxidized, forming a fume which is deposited on adjacent objects.

In order to examine the product of oxidation Berthelot kept a bottle of nickel carbonyl in a double casing of tin plate and succeeded in collecting a few decigrams of a complex oxide, which appeared white in small quantity, but had a greenish tinge when viewed in mass. It was found to be the hydrated oxide of an organo-metallic compound of nickel, and upon analysis gave figures corresponding to the formula  $C_2O_4Ni_3 \cdot 10 H_2O$ . It therefore appears to be the oxide of a complex radical analogous to croconic and rhodizonic acids.

The fact that under ordinary circumstances nickel alone is acted on when a mixture of this metal with any other metallic or mineral substance is treated by carbonic oxide gas, led Mond (J. S. C. I., 1891, 836) to institute experiments to ascertain whether it would not be possible by means of carbonic oxide to extract nickel direct from its ores, and such metallurgical products as nickel speiss and nickel matte. As the nickel is volatilized at the ordinary temperature in the form of a vapor disseminated through other gases from which it can be deposited without first condensing the nickel compound, by simply heating these gases to the moderate temperature of  $200^\circ C.$ , as it is thus obtained in the form of bright coherent masses of great purity, as the carbonic oxide used is completely liberated and can be employed over and over again, and as small quantities of the poisonous nickel compound which may escape decomposition would thus never leave the closed apparatus in which the process would be carried out, it seemed probable that such a process might be capable of industrial application, and might prove more economical than the complicated operations metallurgists have to resort to to produce tolerably pure nickel.

Experiments carried out in conjunction with Langer, with a great variety of nickel ores from all parts of the world, containing from 4 to 40 per cent of nickel, as well as a number of samples of nickel speiss and nickel matte, proved that as long as the nickel is combined with arsenic or sulfur the process was successful. In the majority of cases Mond was able to extract the nickel almost completely in three or four days. Such ores or matte or speiss have in the first instance to be calcined, so as to convert the nickel completely into oxide. The mass is then reduced in a current of hydrogen-containing gases—in practice water gas at a temperature of  $450^\circ C.$  It is cooled down to ordinary temperature and treated with any good apparatus for treating solids by gases. Methodical apparatus moving the reduced ore in opposite directions to the current of carbon monoxide, at the same time exposing fresh surfaces, facilitate the operation. After a certain time the action of the carbon monoxide upon the nickel becomes sluggish. The mass is then heated to about

\* Bull. Soc. Chim. (1892), 434.

350° C. in a current of carbon monoxide, which regenerates the activity of the nickel. This may be done in the same apparatus, but it is preferable to use a separate apparatus connected with the first, and from which the material is returned to the first by mechanical means, so that each apparatus can be kept at the same temperature. The carbon monoxide gas can be employed dilute, as it is obtained from gas producers; but since it is continuously recovered, a purer gas, such as can be cheaply prepared by passing carbon dioxide through incandescent coke, is more advantageous, as it extracts the nickel more quickly and requires smaller apparatus. The gas charged with the nickel compound leaving the apparatus is passed through tubes or chambers heated to about 200° C., in which the nickel is deposited. The gas leaving these tubes is returned to the first apparatus, and circulates continuously. From time to time the nickel is removed from the tubes in which it has been deposited. To facilitate this operation thin nickel sheets, bent to fit the tubes, are inserted, on which the nickel deposits, and which are easily taken out. The metal so obtained is almost chemically pure; only very rarely in the case of certain ores it is slightly contaminated with iron. As the nickel is deposited in perfectly coherent films upon heated surfaces exposed to the gas containing the nickel carbonyl, it was found possible to produce direct from such gas, articles of solid nickel or goods plated with nickel. This result can also be obtained by immersing heated articles in a solution of nickel carbonyl in such solvents as benzole, petroleum, tar oils, etc., or by applying such solution to the heated articles with a brush or otherwise.

Mond \* observes that a mixture of the vapor and air explodes readily but not very violently. The pure liquid does not explode, but at high temperatures it decomposes. The vapor has a characteristic odor and is poisonous. It produces an extraordinary reduction of temperature when injected subcutaneously, sometimes as much as 12 degrees. The liquid can be distilled, but not from solution in liquids of a higher boiling point as decomposition then occurs, finely-divided nickel being separated and carbonic oxide being evolved.

When attacked by oxidizing agents, e.g., nitric acid, chlorine, or bromine or by sulfur, decomposition ensues, nickel salts being formed and carbon dioxide liberated. Metals, alkalis, non-oxidizing acids and the salts of other metals produce no change. Nickel carbonates of composition varying with the hygroscopic state of the atmosphere are formed by exposing the liquid to the action of the air. These precipitates dissolve easily in dilute acid. An intense blue coloration is obtained when nitric oxide is passed through a solution of nickel carbonyl in alcohol (Berthelot).

Nickel carbonyl is very diamagnetic, and an almost perfect non-conductor of electricity (Quinke). All other nickel compounds are paramagnetic. It is opaque for rays beyond the wave length 3820, and its flame gives a continuous spectrum (Liveing and Dewar).

Perkin found the power of magnetic rotation of nickel carbonyl to be greater than that of any other substance he has examined, except phosphorus. Mond and Nasini found the atomic refraction to be about 2.5 times as large as in any other nickel compound, and the former proved it to have great refractive and dispersive powers. The atomic refraction of a liquid ferro-carbonyl bears about the same

\* J. S. C. I., 1892, 750.



ratio to the atomic refraction of other iron compounds. This ferro-carbonyl is similar in preparation and properties to the nickel carbonyl, and at  $180^{\circ}\text{C}$ . the iron is thrown down in bright mirror-like form, carbon monoxide being liberated. Its composition is  $\text{Fe}(\text{CO})_5$ .

To extract nickel from its ores Mond used an apparatus, Fig. 48, consisting of a cylinder divided into many compartments, through which the properly prepared ore is passed very slowly by means of stirrers attached to a shaft. On leaving the bottom of this cylinder the ore passes through a transporting screw, and from this to an elevator which returns it to the top of the cylinder, so that it passes many times through the cylinder until all the nickel is volatilized. Into the bottom of this cylinder carbonic oxide is passed, which being charged with nickel carbonyl vapor leaves at the top, and passes through the conduits shown into tubes set in a furnace, and heated to  $200^{\circ}\text{C}$ . Here the nickel separates from the nickel carbonyl. The carbonic oxide is regenerated and taken back to the cylinder by means of a fan, so that the same gas is made to carry fresh quantities of nickel out of the ore in the cylinder, and to deposit it in the tubes an infinite number of times. When the carbonic oxide comes out at the top of

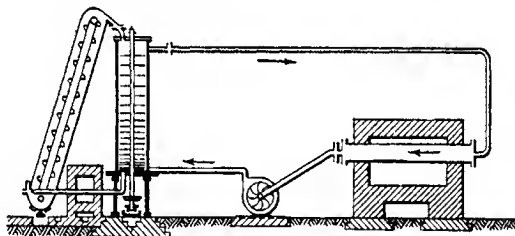


FIG. 48.

the cylinder it passes through a filter to catch any dust it may contain. The carbonic oxide, on escaping from the depositing tubes, is passed through another filter, thence through a lime purifier to absorb any carbon dioxide which may have been formed. By means of this apparatus nickel has been extracted from a great number of ores, in times varying, according to the nature of the ores, from a few hours to several days.

A review by Mond of his experimental work on nickel carbonyl\* is instructive.

\* J. S. C. I., 1895, 945.

Mond stated that "in the course of these experiments finely-divided nickel, formed by reducing nickel oxide at  $400^{\circ}\text{C}$ . by hydrogen, was treated with pure CO in a glass tube, at varying temperatures, for a number of days, and was then cooled down in a current of CO before it was removed from the tube. In order to keep the poisonous CO out of the atmosphere of the laboratory, we simply lit the gas escaping from the apparatus. To our surprise we found that, while the apparatus was cooling down, the flame of the escaping gas became luminous and increased in luminosity as the temperature got below  $100^{\circ}\text{C}$ . On a cold plate of porcelain put into this luminous flame, metallic spots were deposited similar to the spots of arsenic obtained with a Marsh apparatus; and on heating the tube through which the gas was escaping we obtained a metallic mirror, while the luminosity disappeared."

"At the first moment we thought that there must be an unknown element in our nickel giving rise to the production of this effect, but when we examined the mirrors we found them to consist of pure nickel. As it seemed so very improbable that so heavy a metal as nickel should form a readily volatile compound with CO, we purified our CO as perfectly as possible but still obtained the same results."

"We now endeavored to isolate this curious and interesting substance by preparing the nickel with great care at the lowest possible temperature, and treating this nickel with CO at about  $50^{\circ}\text{C}$ ., and thus we gradually increased the amount of the volatile nickel compound in the gases passing through the apparatus. We absorbed the excess of CO by cuprous chloride solution, and thus obtained a residue of several cubic centimeters, containing the volatile nickel compound mixed with a little nitrogen. By passing this gas through a heated tube we separated the nickel, obtaining an increased volume of gas, and found in this a quantity of CO corresponding to about four equivalents for one equivalent of nickel. By further improving our method of preparing the finely-divided nickel and by passing the resulting gas through a refrigerator, cooled by snow and salt, we at last succeeded in liquefying this compound, and were able to produce it with ease and facility in any quantity we desired." Nickel carbonyl "is soluble in alcohol, petroleum and chloroform; it is not acted upon by dilute acids or alkalis, and can be readily distilled without decomposition. But on heating the gas to  $150^{\circ}\text{C}$ ., it is completely dissociated into its components, pure CO being obtained and the nickel being deposited in a dense metallic film upon the sides of the vessel in which it is heated."

"For a long time, while we were engaged in investigating the physical and chemical properties of this interesting substance — which was without parallel in the history of chemistry — and while we were endeavoring to obtain other similar compounds with other metals, I had myself no suspicion that this substance, which was until then only obtainable by very careful and elaborate laboratory manipulations, should ever become available for industrial purposes. But the longer we went on preparing it for our investigations, the more easy we found it to prepare it in quantity, after we once knew exactly the best conditions for so doing. After that I came to the conclusion that it ought to be possible to make use of the ease with which nickel is converted into a volatile gas by CO, while practically all other metals, and notably cobalt (which is so difficult to separate from nickel by other methods), was not acted upon by this gas, for separating nickel from cobalt and other metals on a manufacturing scale, and for obtaining it in a very pure state."

"I erected a plant on a large scale near Birmingham, and after several years of hard work, during which the apparatus has had to be several times reconstructed so as to fulfil all the conditions of this rather delicate process, we have succeeded in our object, and now have for some time produced nickel at the rate of a ton and

a half per week from the Canadian nickel copper matte imported into England. This matte, which contains about 40 per cent of nickel, and an equal quantity of copper, is carefully roasted to drive out the sulfur as far as possible, and is then subjected to the action of hydrogenous gases, either water gas or producer gas, rich in hydrogen, in an apparatus which is called the 'reducer,' the temperature of which is under perfect control, so that 400° C. is never exceeded. From this apparatus the substance, which is now reduced to the metallic state, is taken through air-tight conveyors and elevators into another apparatus called the 'volatilizer,' in which it is subjected, at a temperature not exceeding 80° C., to the action of CO gas."

"This apparatus consists of an iron cylinder, divided into numerous compartments by shelves, and provided with a stirring device, which gradually moves the material from the top to the bottom, while the CO gas passes through in an opposite direction. The CO gas, which should be as rich as practicable, we prepare by passing pure CO<sub>2</sub> through incandescent coke; the pure CO<sub>2</sub> we make by passing the flue gas of a boiler or of a fire through a solution of carbonate of potash, and subsequently boiling the solution. The CO gas, charged with nickel carbonyl, leaving the volatilizer, is passed through a series of tubes or chambers, heated to about 180° C., in which the nickel is deposited in various forms, according to the speed of the gas current, the richness of the gas and the existing temperature. The CO gas, thus almost completely freed from the nickel, is taken back by means of a blower into the volatilizer, where it takes up a fresh quantity of nickel and is constantly used over and over, so that the quantity consumed is limited to the very small amount of unavoidable loss through leakage of the plant."

"The material under treatment is repeatedly taken from the volatilizer to the reducer and vice versa, by means of air-tight conveyors and elevators, until the amount of nickel volatilized begins to fall off. It is then roasted again to remove the sulfur which it still contains, and is treated by sulfuric acid to dissolve part of the copper. The residue, containing nickel, some copper and the other impurities of the matter is again subjected to the previously described treatment until the nickel has been extracted as far as practicable; and the ultimate residue, still containing a few per cent of nickel, is melted up into matte again."

Nickel carbonyl is decomposed \* by passage through a mass of pellets of metallic nickel, heated to about 200° C., causing nickel to be deposited and the pellets to increase in size. The apparatus consists of a vertical cylinder, in which the pellets are placed, with heating spaces formed by an outer casing. A vertical, cooled, perforated tube for the gaseous carbonyl leads from the top down the center of the mass of pellets, nearly to the bottom of the cylinder. To prevent the pellets cohering, they are kept in motion by continuously withdrawing them from the lower end, mechanically screening them with the assistance of worm conveyors, and returning the small ones by an elevator to a feeding hole at the upper end for further treatment with the carbonyl. The pellets which have sufficiently increased in size are passed from the screen and thence through a valved opening into a collecting chamber.

\* Mond, British Patent 1106, Jan. 14, 1898.

In extracting nickel by means of carbon monoxide from mixtures of nickel and other metals, obtained by reducing the mixed oxide with gas containing carbon monoxide, **Fierz** \* displaces the carbon monoxide by hydrogen or removes it by suction from the presence of the reduced metals while the temperature is maintained above that at which nickel will decompose, or combine with, carbon monoxide. The temperature is then reduced to that required for the formation of nickel carbonyl and the gas readmitted.

**Langer** † describes an apparatus for obtaining nickel from nickel carbonyl. Vessels containing the nickel carbonyl are heated by a number of gas flames, each of which is situated in a chamber formed by ribs on the vessel and an outer casing; the liberated gases pass away by an escape pipe, which is surrounded by an annular cooling chamber.‡

**James Dewar** § remarks that the nickel carbonyl vapor at ordinary pressures is very unstable, its components becoming rapidly dissociated with explosion on moderate elevation of temperature, so that its production has hitherto been carried on at a moderately low temperature, such as 50° C. Dewar has found that under considerable pressure, ranging from 2 atmospheres to 100 atmospheres, the compound, either as vapor or as liquid, is much more stable, and therefore higher temperatures can be used in its production, whereby the rapidity of process of manufacture is greatly increased. Thus for the gasification of the nickel a temperature of 100° C. with a pressure of 15 atmospheres is suitable, or a temperature of 180° C. with a pressure of 80 atmospheres. The spongy nickel obtained by the reduction by means of water gas, if treated at the temperature and pressure mentioned, combines rapidly with the carbonic oxide, producing vapor of nickel carbonyl. This vapor, with the excess of carbonic oxide in which it is diffused while still under pressure, on being passed through tubes of a higher temperature, becomes dissociated depositing metallic nickel.||

In the author's laboratory nickel carbonyl has been extensively examined and has proved a satisfactory source of nickel catalyzer. The carbonyl readily decomposes at temperatures between 125° and 180° C. and when decomposed in the presence of oil under some conditions the resulting nickel is very finely divided and imparts to the

\* British Patent 4249, Feb. 19, 1913.

† British Patent 13,350, June 28, 1905.

‡ See also U. S. Patent 815,717, Mar. 20, 1906; 825,844, July 10, 1906; and 865,969, Sept. 10, 1907.

§ U. S. Patent 760,852, May 24, 1904.

|| Electrochem. and Met. Ind. (1904), 291.

oil an inky black color. Even after standing for days or even weeks the nickel remains in suspension. A sample of cottonseed oil carrying about one-half of one per cent of nickel precipitated from nickel carbonyl was exposed to the action of a current of hydrogen gas under practically atmospheric pressure for a period of one hour and a solid product resulted having a melting point of  $47.6^{\circ}\text{C}$ . and a refractive index of 1.4445.



FIG. 49. — Photo-micrograph of Nickel Catalyst derived from Nickel Carbonyl.  $\times 100$ .

The greatest difficulty in the use of nickel carbonyl appears to be the removal of finer portions of the nickel precipitate from the oil after hydrogenation, but this may be accomplished by the observance of due precaution in filtration. The used catalyst recovered by filtration is still active and may be used until its catalytic properties are spent. The spent material may be regenerated more easily than is the case with catalysts consisting of nickel supported on a voluminous carrier of inert material.\*

Another modification of the nickel carbonyl process is described by the author † and involves mixing the requisite amount of nickel carbonyl with hydrogen gas, or water gas, or other gas suitable for the purpose and then passing this mixture into the oil to be treated.

The oil is brought to the decomposition temperature of the nickel carbonyl under these circumstances and the metallic nickel catalyst is liberated in intimate contact with the hydrogen gas, effecting a rapid hydrogenation of the oil.

\*Apparatus adapted for handling nickel carbonyl and hydrogenating oils with the nickel material obtained by its decomposition is shown in U. S. Patent to Ellis, 1,095,144, Apr. 28, 1914.

The oil may contain, if desired, finely-divided solid material to serve as an attaching base for the separated nickel. In case the finely-divided or colloidal nickel which forms is not, after hydrogenation, readily removed by filtration, the oil may be boiled with an aqueous acid solution to remove such nickel material.

Or the oil may be heated to about  $180^{\circ}\text{C}$ ., and atomized with a mixture of hydrogen gas and nickel carbonyl. The nickel carbonyl may be added to the oil and the mixture then atomized with hydrogen gas, the temperature being regulated for the production of the active material. After such atomization the oil may be passed through a heated tube or over a bed of heated fragmental material. Also, the oil may be mixed with a small amount of nickel carbonyl and caused to flow downwardly through a tower containing baffles while hydrogen gas or other gas is allowed to flow upwardly against the downwardly flowing stream of oil. The tower may be heated at one or more points so as to secure a temperature sufficient to decompose the nickel carbonyl and then, if desired, the temperature may be modified so that the mixture on flowing through another portion of the tower is subjected to a temperature better adapted for the hydrogenation process proper.

Nickel carbonyl also may be employed in a different way, in that it may be mixed with asbestos or fuller's earth, or other similar carrier and heated to form catalytic nickel without resorting to direct reduction of say nickel oxide by hydrogen. Such a catalytic body may then be used for treating oils in the presence of hydrogen under suitable conditions of temperature and pressure.

In the case of oleic acid or other bodies which may be converted into a vapor form, the nickel carbonyl and hydrogen may be mixed with the vapors of such bodies and passed through a heating zone, preferably being raised to a temperature of  $180^{\circ}$  or  $200^{\circ}\text{C}$ ., or to whatever temperature under the particular conditions of operation is required for a satisfactory decomposition of the carbonyl compound into an active body. In this case also nascent nickel is liberated in the presence of hydrogen to good advantage.\*

Lessing † uses nickel carbonyl in the hydrogenation of unsaturated substances. (See page 42.)

Fig. 49a is a view of a hydrogenating apparatus suggested by Lessing and Fig. 49b represents a section of the upper portion of the hydrogenating vessel showing a spraying nozzle through which the liquid to be treated may be forced. A is the vessel in which hydrogenation occurs. The substance to be hydrogenated is pumped from a supply tank through a pre-heater contained in a tank C, into vessel A which is heated by a steam jacket. The hydrogenated substance is forced by the pressure from vessel A into the tank C where it is used as heating agent. If finished it is run off; if not finished, it is returned by the circuit shown. The gases enter on the right, are compressed by compressor D, and forced through the volatilizer E, passing therein over reduced nickel. The gases issuing from volatilizer E and containing nickel carbonyl then enter vessel A. The gases left unabsorbed and now free from nickel issue from the

\* See also U. S. Patent to Ellis, No. 1,138,201, May 4, 1915, and 1,251,202, Dec. 25, 1917.

† U. S. Patent No. 1,162,623, November 30, 1915.

vessel *A* through the right-hand outlet at the top of *A* and are passed through cooler *F* and can be either discharged or returned into circulation. Any oil carried along with the gases is deposited in the cooler *F* and may be run off. If the compound to be treated is in the state of gas or vapor, as for instance, in the hydrogenation of the more volatile tar oils, it is simply mixed with the hydrogen containing the nickel carbonyl and subjected to the temperature required for hydrogenation. Likewise in the case of a liquid some hydrogen may be mixed with the liquid, a spray being then formed by injector action instead of by liquid pressure.

Crossley \* refers to British patent to Lessing, 18,998, of 1912, and states that the process described therein appears to differ materially from others, more particularly in the novel method for bringing catalyst and oil in contact. According to this

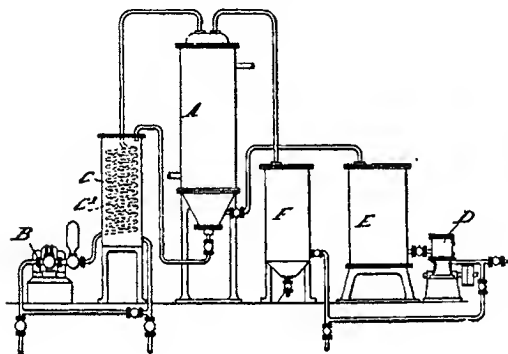


FIG. 49a.

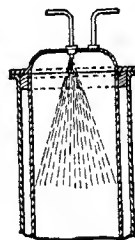


FIG. 49b.

process hydrogen containing 5 to 10 per cent of carbon monoxide, such as may easily be prepared from water-gas or the thermal decomposition of coal gas or hydrocarbons, is passed over reduced nickel, with formation of nickel carbonyl. The nickel need not be pure, but in the form of such complex mixtures as are obtained in the treatment and reduction of nickel ores. The mixture of hydrogen and any desired proportion of nickel carbonyl is then passed into the substance to be hydrogenated at a temperature between 200° to 240° C. when the nickel carbonyl is decomposed and elementary nickel, in a very pure and particularly active form, is produced. The proportion of nickel carbonyl required is very small, excellent results having been obtained with an amount equivalent to 0.1 part of nickel in per 100 parts of oil. Fresh nickel carbonyl is always passing into the substance to be hydrogenated, and the nickel is believed to act in the nascent condition at the moment of decomposition of the nickel carbonyl. This he states seems to be borne out by the fact that if the same percentage of nickel be introduced into an oil as nickel carbonyl, the latter decomposed and then hydrogen passed in, there is practically no result from the commercial point of view.

\* Pharm. Soc., Apr. 21, 1914; Pharm. J., 1914, 92, 604, 637 and 676; J. S. C. I., 1914, 1135.

George Schicht A.-G. \* recommends a form of nickel kieselguhr catalyzer prepared from nickel carbonyl. The carbon monoxide required may be obtained from water gas by the Linde-Caro process.

The catalytic material is prepared in the following manner: Carbon monoxide is conducted under pressure over finely-divided nickel which is heated in a retort and the nickel carbonyl which is formed is cooled below its boiling-point. Purified kieselguhr is placed in a nickel vessel, the nickel carbonyl is added and the mixture heated to cause metallic nickel to form by decomposition of the carbonyl. The carbon monoxide liberated is removed and can be used again to form nickel carbonyl. The last traces of carbon monoxide or undecomposed nickel carbonyl which may tend to effect the progress of reduction injuriously are removed through treatment with hydrogen, carbon monoxide or other indifferent gas. The nickel kieselguhr material is warmed during this stage of the process. The product is ground with oil with exclusion of air affording an "emulsion" or pasty composition which is used as a source of catalytic material. In place of oil, any suitable liquid vehicle may be used. The product is stated to be of such a character that when mixed with oil it does not lump together or deposit on the bottom of the vessel. The regeneration of spent catalyzer is simple, for, after the removal of the oil, it is stated that the nickel may be again directly converted into nickel carbonyl and decomposed as before. The residue of kieselguhr from which the nickel has been removed as the carbonyl may likewise be utilized as a carrier.

In a publication by Coleman entitled "The Nickel Industry" issued by the Canadian Department of Mines, 1913, 153, a very complete description of operation of the nickel carbonyl process for producing nickel, as carried out at the Mond plant, Clydach, Wales, is given.

\* Austrian Patent No. 70,771; Seifen. Ztg., 1916, 169.



## CHAPTER X

### THE RARE METALS AS CATALYZERS

As a catalyzer in this field palladium has received considerable study, for, in spite of high first cost, its pronounced effectiveness, together with its ability to effect hydrogenation at relatively low temperatures, makes it particularly attractive.

Many years ago, Fokin \* stated that he regarded palladium as the most powerful of all catalyzers, having found that reduction takes place readily at 80° to 90° C., while with nickel, a temperature of 180° to 200° C. was necessary for practical hydrogenation. Fokin's experiments at that time were concerned with electrolytic reduction. By this means he reduced linseed, wood, castor and cod liver oil. He found that while *palladium* black would reduce oleic acid completely to stearic acid, *platinum* black under the same conditions gave only 24 per cent of stearic acid.

Paal † worked with colloidal palladium preparations and hydrogenated castor, olive, fish oil and animal fats. He found that sesame oil, after hydrogenation, showed the Baudoin reaction only very faintly, while cottonseed oil no longer responded to the Beechi and Halphen reaction. Skita has worked with palladium incorporated with a protective colloid.

Paal recommends ‡ platinum or palladium chloride admixed with a neutralizing agent such as sodium carbonate. He states that the reduction of fats and unsaturated fatty acids of animal and vegetable origin may be effected by allowing hydrogen to act on these, in presence of platinum metals, or protohydroxide compounds of the latter, which have been deposited upon certain finely-divided substances and act as catalyzers or carriers of hydrogen. It has also been ascertained that the reduction of the fats and fatty acids may be effected by hydrogen in presence of solid salts of the platinum metals. Both the simple salts, such as palladium protochloride ( $\text{PdCl}_2$ ), platinum protochloride ( $\text{PtCl}_2$ ), platinum chloride ( $\text{PtCl}_4$ ), platinum hydrochloride ( $\text{H}_2\text{PtCl}_6$ ), platinum sulfate and the double salts, for instance potassium

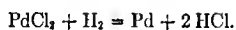
\* Chem. Ztg. [2], 1906, 758; [1], 1907, 324.

† Ber., 41, 2282.

‡ U. S. Patent 1,023,753, April 16, 1912.

chloroplatinate ( $K_2PtCl_6$ ), copper platinochloride, may be used. When the double salts are used, care must be taken that no anticatalytic substances, such for instance as lead, find their way into the reduction mixture. Use may be made of salts whose acid radicals or other constituents are themselves reduced by hydrogen, for example acid platinous oxalate. In all cases the method is simple; and it is distinguished from those in which the finely-divided metals are used by the omission of the preparation of the finely-divided platinum metals or their protohydroxides and of the deposition on special carriers.

The salts in a crushed condition, preferably in the state of powder, are mixed with the fats or fatty acids to be hydrogenated; and hydrogen is allowed to act on this mixture, with stirring, at temperatures below 100 degrees preferably under a pressure of several atmospheres. In a short time the solid reduction product of the fat or fatty acid will be obtained. All that is necessary to insure the action of the solid salts of the platinum metals is that they must be present in the solid form during the progress of the reaction. The salts may also be added to the fats in a dissolved condition (for example in aqueous solution), the solvent being evaporated before or at the beginning of the reduction process. A suspension of the solid salts may also be used. For example, the salts of the platinum metals may be triturated with a portion of the fat or oil that is to be reduced, the mixture being then added to the main portion of the fats or fatty acids to be reduced. Or a suspension of the salts in mineral oil may be prepared, and this mixture may be added to the substances that are to be reduced, in which case the suspensory medium may be eliminated during the process of reduction. A single salt of a platinum metal may be used, or several salts, and even several platinum metals may be mixed together; and the salts may also be used in conjunction with the platinum metals which have been deposited on carriers, devoid of anticatalytic action, such as copper, or magnesium carbonate. It is probable that, during the process, the salts of the platinum metals are split up into metal and free acid, for example:



In any case, however, the solid platinum metal salts greatly facilitate the absorption of hydrogen by fats and fatty acids. Very small quantities of the platinum-metal salts are sufficient to reduce large quantities of fat or fatty acids in presence of hydrogen. When the reduction process is completed, the platinum metals or their compounds can be easily separated from the reduced fat or fatty acid by filtration, and used again.

To prevent the formation of free acid, as, for example, hydrochloric acid from the chlorides of the platinum metals, in the reducing process, there is added to the powdered platinum salt a neutralizing agent, such as anhydrous soda, in sufficient quantity to combine with the liberated acid. The employment of salts of the platinum metals assists the reduction process considerably more than is done by palladium black or platinum black containing an amount of platinum metal equal to that in the platinum metal salts used in the present method. Thus, for example, 1.7 parts of  $PdCl_2$  (= 1 part of Pd) in presence of hydrogen will convert 10,000 parts of fat or fatty acid into solid masses within 3 or 4 hours. If, however, the  $PdCl_2$  be

replaced by a quantity of palladium black containing the same amount of palladium, then, with a ratio of 1 part of Pd to 10,000 parts of fat or fatty acid, these substances, according to Paal, will remain liquid, even when the palladium and hydrogen are allowed to act for twice or three times as long as with  $\text{PdCl}_2$ .

Paal notes that the time required for the reduction depends on the amount of the platinum metal salt used, and on the pressure under which the hydrogen is allowed to act. By using a palladium salt as the hydrogen carrier, about 50,000 parts of fat or unsaturated fatty acid can be hydrogenated within from 6 to 8 hours with a quantity of salt, for example,  $\text{PdCl}_2$ , corresponding with 1 part of Pd.

Paal gives the following example: One million parts by weight of castor oil or oleic acid are treated with thirty-four parts by weight of dry palladium protochloride (= 20 parts of Pd) in the form of powder, with or without the equivalent amount of anhydrous soda; or with 140 parts by weight of dry platinum protochloride (= 100 parts of Pt) in the form of powder; or 172 parts of platinum chloride; or 230 parts of platinum hydrochloride, with or without addition of an equivalent amount of anhydrous soda. The mixture is placed in a pressure vessel, from which the air is exhausted as completely as possible, and hydrogen is then admitted into the vessel under a pressure of 2 to 3 atmospheres. The reduction mixture is kept in motion by a stirring apparatus. The vessel is heated to about  $80^\circ \text{C}$ . although the reduction may also be carried out at a lower temperature. The progress of the reduction and the consumption of hydrogen is revealed by the fall in pressure as indicated by the pressure gauge. When the gauge registers only a low pressure, a fresh quantity of hydrogen is admitted. The completion of the reduction process can be recognized by the gas pressure remaining constant for some considerable time. When the reduction is ended, the reduction product is freed from the catalyzer in a filter press which is adapted to be heated.

The work in the field of catalytic reduction of organic compounds has been rather comprehensively covered in a publication by Skita entitled "Über Katalytische Reduktionen Organischer Verbindungen" (Stuttgart, 1912). Skita has taken out a patent assigned to Boehringer and Son \* which is concerned with the hydrogenation of organic compounds with the aid of catalyzers consisting of salts of the platinum group of metals. The protective colloid previously employed he now finds to be unnecessary. He states he has found that an unsaturated substance can be hydrogenated when there is added to it, or its solution or suspension, a small amount of palladium chloride or any other soluble salt of a platinum metal and the whole exposed to hydrogen, most advantageously under pressure. The addition of an acid is usually advantageous in this operation and hydrochloric acid is recommended; but with fatty bodies it suffices merely to add a simple aqueous solution of a compound of a metal of the platinum group. As an example, he states, that 50 grams of olive oil may be suspended in a solution containing about 0.05 gram of platinum chloride, 20 cc. of alcohol, 50 cc. of water and 8 cc. of dilute hydro-

\* U. S. Patent 1,063,746, June 3, 1913.

chloric acid. After treatment with hydrogen at a pressure of about 4 atmospheres and at a temperature of 70° C. a solid fat results. In another example about 250 grams of castor oil is well mixed with a solution of about 0.05 gram of palladium chloride in 5 cc. of water. The whole may then be treated at about 70° C. in an autoclave with constant stirring, with hydrogen under a pressure of 4 atmospheres. After two and one-half hours the oil will be found so far hydrogenated that it will solidify to a hard mass on cooling.\*

In an address before the Chemical Society of Karlsruhe Dr. Skita made the following comments on the hydrogenation of organic material.†

He stated that the acceleration which various reactions experience in the presence of catalyzer is the more rapid the greater the surface of the catalyzer. As a result a catalyzer in solution is always more active than is the case when the catalyzer is in a finely-divided or precipitated state. This especially is true with metals of the platinum group which exert an action of a very marked character when in solution in the colloidal condition.

Colloidal platinum was first produced by Bredig by the action of an electric current on metallic platinum in aqueous or ethereal solution. Bredig recognized the property which these colloidal solutions possessed of serving as a carrier for hydrogen and he in fact reduced nitrous acid to ammonia. Such colloids are not reversible, that is to say if the colloidal solution is evaporated to dryness the metal will not again go into solution. A metal colloid which is easily soluble in water was discovered by Paal who made use of a water-soluble protective colloid, namely, the sodium salts of protalbinic or lysalbinic

\* The hydrogenation of unsaturated substances is effected, according to Skita, by treatment with hydrogen in the presence of small quantities of compounds of metals of the platinum group in solution. The substances to be hydrogenated may be dissolved or suspended in a liquid (French Patent 447,420, Aug. 20, 1912; also British Patent 28,754, Aug., 1912, and addition to the latter Patent 18,996 (1912). A solution of palladium chloride acidulated with dilute hydrochloric acid was used by Skita as a catalytic solution for the treatment of camphene. Hydrogen was used under a pressure of one atmosphere. The hydrogenation of olive and castor oil in this manner is described. In the addition patent Skita states that the employment of dilute acid is not always necessary since in many cases the reaction can be carried out simply by passing hydrogen through a mixture of the substances to be reduced and a solution of the salt. J. S. C. I., March 15, 1913, 253.

Skita (Chem. Zeit. Rep. (1913), 680; British Patents 18,996, 1912, and 16,283, 1913) carries on reduction processes without the addition of any acid to a solution of a salt of the platinum group and also makes use of colloidal solutions of an hydroxide of the platinum group as a catalyzer.

† Seifen. Ztg. (1913), 960.

acids, to maintain the metallic platinum or palladium in a water-soluble condition.\*

With colloids of this character prepared from palladium Paal succeeded in adding hydrogen to a large number of unsaturated aliphatic compounds which were soluble in water or dilute alcohol. For the reduction of many organic compounds, such as acids, bases and hydrocarbons, the presence of acid material is of importance and accordingly Skita has used an acid-stable protective colloid such as gum arabic in place of the sodium salts mentioned above. If gum arabic is added to a solution of platinum chloride, no platinum hydroxide is precipitated when carbonate of soda is added to the solution, for the platinum remains suspended in the colloidal condition.

By careful evaporation platinum compounds may be obtained as black plates or scales which are soluble in water and dilute acids. When these colloidal solutions of the hydroxide are agitated in the presence of hydrogen a very acid-resistant form of colloidal platinum results. On evaporation a form of platinum is obtained which is easily soluble in water. All such platinum and palladium compounds are eminently adapted to catalytically transfer hydrogen to unsaturated material contained in an acid or neutral vehicle. It is especially easy to add hydrogen to the double bonds of aliphatic and hydrocyclic hydrocarbon compounds. This is the case as regards the reduction of alkaloids.

Another interesting observation is that very stable colloidal solutions of platinum may be obtained readily by passing hydrogen through such colloidal solutions of platinum containing gum arabic, even when the solution is cold. In a similar manner colloidal solutions of palladium are produced from palladium chloride.

Finally it may be mentioned that in this way hydrogen may be added to aromatic and heterocyclic compounds which cannot be hydrogenated with platinum black catalyzer.†

\* Colloidal solutions of gold, silver, platinum, palladium, copper, lead, iron, zinc, tin, nickel, aluminum, magnesium, bismuth, antimony and cadmium, respectively, have been prepared with great ease by an electrical disintegration method, using a high-frequency alternating arc, the leads to which were taken from two points on the inductance of the oscillatory circuit of a Poulsen arc as used in wireless telegraphy. By varying the conditions it was possible to obtain currents of from 0.14 to 15 amperes and E.M.F. of 480 to 4080 volts, and colloidal solutions showing a wide range of colors were thus obtained from a number of the metals. (Morris-Airey and Long, *Proc. Univ. Durham Phil. Soc.* (1912-1913), 5, 68; *J. S. C. I.* (1913), 1015.)

† In his dissertation entitled "Über katalytische Hydrierungen organischer Verbindungen mit kolloidem Palladium und Platin," Meyer draws the following con-

Colloidal suspensions of the metals \* have proved excellent catalyzers, effecting many of the reactions which are brought about by enzymes. The analogy between the action of the finely-divided metals and the organic enzymes is strikingly illustrated by the behavior of poisons on the two. The same substances which poison the ferments and which retard the rate at which they decompose hydrogen dioxide, also poison platinum and retard the rate at which it effects the same decomposition. Thus mercuric chloride and hydrocyanic acid in the merest traces poison the organic enzymes. The same quantities produce almost exactly the same effect on the finely-divided metals, with respect to their power to decompose hydrogen dioxide.†

clusions. Methods of reduction depending on the use of a solution of palladious chloride and gum arabic in water-alcohol mixture, forming colloidal palladium with hydrogen, do not progress satisfactorily unless bodies are present which are capable of forming addition compounds with palladious chloride. The action of hydrogen on a hot solution of palladium chloride and a protective colloid gives rise to a colloidal solution of palladium. From colloidal palladium or platinum solutions using gum arabic or gelatine as a protective colloid, the corresponding reversible metal colloid is obtained. With the aid of gum arabic or gelatine as a protective colloid it is possible to obtain permanent colloidal solutions of palladium and platinum hydroxide. By careful evaporation and drying of these colloidal solutions solid products are obtained which may be brought again into colloidal solution by peptization. Stable colloid solutions of palladium may be advantageously obtained by the reduction of dialyzed colloid palladious hydroxide solutions. For the production of a colloidal solution of platinum it is recommended that reduction of chlorplatinic acid by hydrogen in the presence of a protective colloid be employed, in which case the mixture should first be inoculated with small amounts of colloidal platinum or palladium. Colloidal solutions of platinum and palladium with gum arabic or gelatine as a protective colloid are well adapted to the hydrogenation of olefine bodies. The hydrogenation of aromatic bodies with colloidal metallic platinum is possible only in strong acetic acid solutions. The hydrogenation of aromatic bodies is carried out more easily with platinum than with palladium. While gum arabic is suitable for use as a protective colloid with platinum or palladium in the hydrogenation of certain organic bodies, it is found that gelatine under some conditions acts as a catalyzer poison. Vulcanized rubber also affects the activity of the catalyzer. The inoculation method for the production of colloidal solutions of platinum affords a convenient laboratory procedure for the hydrogenation of aromatic bodies as the formation of the colloidal solution and the process of hydrogenation follow one another quickly. The hydrogenation of aromatic bodies using colloidal platinum as a catalyzer progresses three or four times quicker than when platinum black is employed. See also J. S. C. I. (1913), 46, and Ber. (1912), 45, 3379.

A solution of colloidal platinum is capable of causing the union of hydrogen and oxygen. (Ernst, *Zeitsch. physikal. Chem.* (1901), 37, 448.) Ethylene unites with hydrogen even in the cold, in the presence of platinum sponge. (De Wilde, Ber. 7, 354.)

\* Jones, *A New Era in Chemistry*.

† Measurements have shown that the decomposition of hydrogen dioxide by metals

**Karl**\* has studied with considerable care and in a quantitative way the action of palladium supported on various bodies. He found that palladium precipitated on finely-divided nickel or magnesium proved effective catalytically, while if precipitated on lead, aluminum, iron, or zinc, little or no hydrogenation was effected, owing to the anticatalytic action of these metals. While metallic zinc is anticatalytic, zinc oxide and carbonate have no such effect. In these investigations Karl worked principally with fish, cotton and castor oil and oleic acid.†

is a reaction of the first order, that is, the metal, strictly speaking, does not enter into the reaction at all, only the mass of hydrogen dioxide present undergoing change.

A hydrogenizing ferment in the animal organism capable of transforming nitrobenzene into aniline has been observed by Abelous and Gerard (*Comptes Rend.*, 130 (7), 420). A clear aqueous extract of horse's liver, in presence of chloroform and in an atmosphere of hydrogen, reduced nitrobenzene to aniline, while the same extract, previously boiled, was without action. Abelous and Gerard have previously shown (*J. S. C. I.*, 1899, 871) the deoxidizing action of this ferment, but have had no instance of hydrogenation under its influence. (See also Chandler, *J. S. C. I.*, 1913, 73.)

\* Inaugural Dissertation, Erlangen, 1911.

† Paal and Karl (*Ber.* (1913), 3069; *Chem. Ztg. Rep.* (1913), 642) tested palladium on various carriers as catalytic material for hardening fats and have found that the oxides, hydroxides and carbonates of lead, cadmium, zinc, aluminum and iron have an anti-catalytic action similar to the metals which they contain. The corresponding compounds of nickel and cobalt, and also magnesium oxide, were investigated. These carriers were coated with palladium by mixing with a solution of palladium chloride in a weak aqueous solution of hydrochloric acid at room temperature, or slightly warmed. Palladium hydroxide was thus precipitated and reduction was obtained by treatment of the powder, which was first moistened with ether, to the action of hydrogen at room temperature. The catalyzer was mixed with fatty material without permitting contact with the air and reduction was carried out in an agitator in an atmosphere of hydrogen. Magnesium oxide did not retard the catalytic action of palladium. In fact, the reduction process appeared to be somewhat increased by the presence of this material.

Paal and Windisch carried on similar experiments with platinum. (*Ber.* (1913), 4010.) Metal powders of various sorts were purified with alcohol and ether and then platinized by shaking with a solution of chlorplatinic acid. Metallic oxides and carbonates were platinized by the action of sodium carbonate and hydrazine hydrate on a solution of chlorplatinic acid containing the oxide or carbonate in suspension. These products as catalyzers in the hydrogenation of cottonseed oil were found to have differing degrees of catalytic action, and only nickel and magnesium had no influence on the activity of the platinum. The platinum was much less active in the presence of aluminum, cobalt and bismuth, and was rendered completely inactive by iron, copper, zinc, silver, tin and lead. Of the oxides and carbonates examined, only the magnesium compounds were without influence.

Wieland (*Ber.* (1912), 45, 2615) considers palladium black less sensitive to "poisons" than platinum black, for in presence of the former a sample of benzene containing thiophen absorbed hydrogen at a noticeable rate although not so rapidly as pure benzene.

A long list of salts available as catalyzers is given in German Patent 260,885 \* embracing the sulfates, nitrates and chlorides of platinum and palladium, and double salts of these with alkali chlorides and other chlorides, also certain complex compounds of these metals. The salts are added in an undissolved state directly to the oil to be hardened and subsequently a neutralizing agent also undissolved is added. The temperature is maintained below 100° C. When employing double salts care should be taken to have no anticatalytic substances, such as lead, present in the mixture. Salts, such as acid oxalate of platinum, whose acid radical is capable of reduction, may be used.† If necessary, a solid neutralizing agent may be added (cf. Pual).

The Seifenseider Zeitung, 1912, 550, makes mention of a German Patent application for a process of making hardened fats, using as catalyzers platinum and platinum hydroxide in the form of precipitates and on inert carriers in place of the corresponding compounds of palladium.

In order to avoid the accidental introduction of air or mercury when reducing by means of hydrogen and colloidal platinum a special apparatus has been constructed by Stark (Ber. 1913 (46), 2335). It consists of a glass vessel with two necks, each provided with a glass stopcock. A small funnel with a stopcock is fused into the upper part of the vessel between the two necks. One neck is connected with the source of hydrogen, the other with a graduated gas burette and mercury reservoir. The substance to be reduced is placed in the glass vessel and a current of hydrogen passed through. At this stage the burette and reservoir contain no mercury. The hydrogen supply is then cut off and mercury is poured into the reservoir from which it flows and partly fills the burette. By lowering the reservoir a solution of platinum or palladium can be introduced through the funnel with the stopcock without admitting any air.

Lehmann carries out the hydrogenation of oils or unsaturated fatty acids by passing hydrogen through oil containing a small amount of osmium tetroxide, while the oil is being heated. Osmium dioxide forms from the tetroxide, producing a colloidal solution which can be removed by animal charcoal. In one experiment 10 grams olive oil

Cf. Windisch, Ueber die Hydrogenisation ungesättigter organischer Verbindungen durch Platin und Palladium-wasserstoff und die antikatalytische Wirkung von Fremdstoffen auf den Hydrogenisierungsprozess. Erlangen, 1913.

Dissertation: Schwarz, Erlangen, 1913, publishes work on colloidal platinum and the effect of anti-catalytic bodies. J. v. Bergen, Karlsruhe, 1913, gives results of work with palladium hydrosols.

\* Seifen. Ztg., 1913, 851.

† Fokin has used the compound  $\text{PdCl}_2 \cdot 2 \text{NaCl}$  as a catalyzer (Russian Patent 22,629, Sept. 30, 1912; Chem. Ztg. Rep., 1914, 40).



with 0.05 gram osmium tetroxide produced in  $1\frac{1}{2}$  hours a fat of melting point  $39^{\circ}\text{C}$ . It is not necessary to use hydrogen under pressure.\*

Besides palladium and platinum the metals iridium, rhodium, ruthenium and osmium are specified as catalytic material.† Madina-veitia‡ has studied the catalytic activity of ruthenium, rhodium, iridium and osmium black.

In connection with the volumetric determination of hydrogen by catalytic absorption in a solution of sodium picrate and colloidal palladium Paal and Hartmann § note that oxygen and unsaturated hydrocarbons must be removed, for in presence of palladium, hydrogen reacts with them to form water and paraffin hydrocarbons respectively; and carbon monoxide should also be removed, as it acts as a "poison" on the catalyst, and greatly retards the absorption.

Colloidal solutions of hydroxides of metals of the platinum group, obtained by treating a solution of a salt of the metal with sodium carbonate in presence of gum arabic, are found by Skita (British Patent 16,283, July 15, 1913) to be efficient hydrogen carriers in the hydrogenation of unsaturated compounds, the reaction being possible even in neutral solutions. In this manner it is stated that unsaturated fatty acids or fats can be hydrogenated to any degree. For example, a hard fat is obtained by passing hydrogen at a pressure of seven atmospheres into a mixture of 50 parts (by weight) of peanut oil and 60 parts of a colloidal solution of palladium hydroxide, containing about 0.07 part of the hydroxide, at a temperature of  $60^{\circ}\text{C}$ .

\* Arch. Pharm. (1913), 152; Seifen. Ztg. (1913), 418.

† Vereinigte Chemische Werke A. G. French Patent 425,729 (1911); Seifen. Ztg. (1912), 390.

In using platinum or palladium the following example is given: 1000 kilos castor oil are mixed with 1 kilo of catalyzer which contains 1 per cent of palladium or 2 per cent platinum either in the metallic state or in the form of the lower hydroxide. This mixture of oil and catalyzer is placed in a closed receptacle equipped with an agitator. Any moisture present is removed as completely as possible and then hydrogen is introduced, creating a gas pressure of 2 to 3 atmospheres. The contents of the receptacle are heated to  $80^{\circ}\text{C}$ . and the agitator put into operation. Hydrogen is introduced as required. The hydrogenation of fatty acids may be carried out in a similar manner, but care should be taken to use catalytic material containing palladium or platinum which is not attacked by acids. One composition mentioned for the purpose is prepared by mixing barium chloride with palladium or platinum chloride to which is added sodium sulfate and some hydroxylamine or other reducing agent. For the production of oleic acid one part of catalyzer carrying 1 per cent of palladium or 2 per cent platinum is used to 1000 parts of the fatty acid.

Palladium in various metallic forms as a catalyzer is mentioned in Seifen. Ztg. (1914), 7, as forming a basis of a patent application by the Naamlouze Vennootschap Ant. Jurgens Vereenigde Fabrieken. See German Patent 272,340, 1912.

‡ Chem. Abs., 1914, 1106.

§ Ber. (1910), 43, 243.

**Thron** \* adds hydrogen to unsaturated bodies with the aid of a finely-divided metal of the platinum group and formic acid. The latter is split by the platinum metals by catalytic action into carbonic acid and hydrogen, the latter, it is stated, causing the formation of a compound of the platinum metal and hydrogen (hydride of the platinum metal). By adding to the substance to be hydrogenized formic acid and, for example, palladium black, the development of carbonic acid begins at once, while hydrogen is combined with the unsaturated bodies present.

A platinum catalyzer used by **Porter** (U. S. Patent 684,863, Oct. 22, 1901) for igniting combustible gas is prepared by mixing platinum black with the oxide of zirconium in about the proportion of twenty-five per cent of platinum to seventy-five per cent of zirconium oxide. To prepare this, the platinum in a state of solution is mixed with the oxide of zirconium and the liquid is evaporated, leaving the platinum compound distributed throughout the mass. This is then applied to some incombustible substance, such as asbestos or mineral wool, which forms a convenient support for the substance. After heating, the platinum remains in a finely-divided state. **de Montlaur** used mica as a support for platinum, *Zeitsch. f. angew. Chem.* (1914), 61, No. 7.

A catalyzer capable of bringing about reaction between air and ammonia to form nitric oxide has been proposed by **Schick** (U. S. Patent 971,149, Sept. 27, 1910) and is based on the use of platinum coated on a suitable carrier such as quartzite, porcelain and the like. The spongy form of platinum is not useful for the purpose, owing to undesirable side reactions taking place in the center of the spongy mass. Accordingly a very thin surface layer of platinum is deposited on the carrier, and to get a coating of sufficient thickness the carrier is coated with a glaze such as a mixture of felspar and an alkali that will soften easily when heated. The platinum material is then baked on the carrier in the presence of this glaze which brings about the formation of a uniformly thin layer of the metal. A temperature of 1400° C. is used.

In discussing the properties of platinum as a contact material for igniting combustible gas, **Perl** (U. S. Patent 615,363, Dec. 6, 1898) states that after the discovery that finely-divided platinum did not fulfil the requirements, the endeavor was made to increase the effect of the finely-divided platinum by mingling the same with different porous bodies, according to the suggestion of **Liebig** (*Pogg. Ann.*, Vol. 17 (1829), 107). **Dobereiner** (*Journ. Praktischer Chemie*, 1839, Vol. 17, 158) went further and prepared finely-divided platinum within the pores of natural or artificial meerschaum or clay. **Perl** regards a method of this character to bring about the formation of chloride of magnesium or other earths, because by reduction of the platinum salts which are in the pores of the employed material a part of the latter is always transformed by the action of the acids freed from the platinum salts (chiefly hydrochloric acid) into compounds which are injurious on account of their hygroscopic properties, and which act as fluxes, causing the igniting material to become denser and more impenetrable for the gas after a short time. To meet these objections **Perl** proceeds as follows:

Porous combustible material is thoroughly mingled with a solid or dissolved platinum salt. The mixture is dried at a moderate temperature, and the platinum

\* U. S. Patent 1,077,442, Nov. 4, 1913.

is reduced in the pores of the incombustible material by bringing the mixture to a high degree of heat in a covered crucible until the hydrochloric acid or the vapors of any other acid have disappeared. The same result is also brought about by heating the mixture in a reducing gas flame. The residual salts are now extracted with diluted hydrochloric acid and subsequently with water until all trace of any soluble salts removed.

Efrem (British Patent 14,339, 1899; J. S. C. I., 1900, 726) and Chem. Fab. vorm. Goldenberg (British Patent 618, 1900; J. S. C. I., 1901, 250) employ clay and similar supporting material for platinum in preparing catalytic material. (See also British Patents 6448, 1905; J. S. C. I., 1906, 432 and 10,729, 1901; J. S. C. I., 1902, 548.)

C. E. Munroe (U. S. Patent 724,317, March 31, 1903) produces a form of platinum contact material active in oxidation processes by causing the formation upon perforated sheets or disks of asbestos and upon sheets or disks of perforated metal or woven wire of a coating of finely-divided platinum. For instance, a perforated sheet of asbestos is immersed in an alcoholic solution of ammonium chloride and then in an alcoholic solution of platinic chloride, or, if preferred, the sheet may be first immersed in the platinic chloride and subsequently in the ammonium chloride, forming upon the surface of the asbestos a crystalline precipitate of ammonium-platinic chloride. When the precipitate has been formed, the sheet of asbestos is heated. The heat acts first to drive off the alcohol and then decomposes the double platinum salt, leaving the metal in a very finely-divided state.

Paal and Amberger \* describe the production of preparations of a greasy consistency containing inorganic metal colloids of the platinum group, consisting in incorporating solutions of the divalent salts of the metals of the platinum group with bodies maintaining colloids in the colloidal state (protecting colloids) especially with wool fat or the alcohols obtainable therefrom by saponification, and adding a carbonate of an alkali to form the colloidal lower hydroxides of the metals employed. They note that preparations containing combinations of the divalent salts of the metals of the platinum group in a colloidal condition can be obtained, if, instead of the alkali carbonates used above, the alkali salts of certain weak organic acids are selected, for instance, the salts of the higher, saturated, or unsaturated, fatty acids (soaps). In this way there are produced in the presence of solutions of the metal salts, for instance, of divalent palladium, or platinum, triturated with wool fat, products which contain the corresponding palladium, or platinum, salts dissolved in colloidal form in the wool fat.

If, according to Paal and Amberger, wool fat be impregnated with a concentrated aqueous solution of palladium chloride ( $\text{PdCl}_2$ ) and the mass be then triturated with the equivalent quantity of potassium oleate in concentrated aqueous solution, the salts mutually decompose with formation of potassium chloride and palladium oleate which remains dissolved in colloidal form in the wool fat. As the palladium chloride is difficultly soluble in pure water but readily in hydrochloric acid it is dis-

\* U. S. Patent 1,077,891, Nov. 4, 1913.

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solved in the latter and the acid is neutralized before triturating the liquid with wool fat by means of an amount of sodium carbonate equivalent to the hydrochloric acid used. The neutral  $\text{PdCl}_2$  then remains dissolved in the liquid.

In order to obtain a preparation containing about 25 per cent colloidal palladium oleate 0.85 part of palladium chloride  $\text{PdCl}_2 = 0.5$  part of palladium are dissolved with the application of heat in 0.45 part of fuming hydrochloric acid (38 per cent  $\text{HCl}$ ) and 2 parts of water, and the hydrochloric acid is neutralized by the addition of 0.3 part of anhydrous soda either solid or dissolved in 0.7 part of water. The solution of  $\text{PdCl}_2$  thus obtained is then triturated intimately in small portions with 9.5 parts of wool fat softened at a gentle heat. Into the body thus obtained are then stirred, also in small portions, 3.5 parts of potassium oleate dissolved in 15 parts of water. The formation of the palladium oleate is detected by the fact that the greasy mass colored red-brown by the palladium chloride becomes, on being triturated with the potassium oleate, first yellow-brown, then gray-brown and, after being allowed to stand some considerable time, black-brown. To purify the product it may be either treated repeatedly with hot water at from  $50^\circ$  to  $60^\circ \text{C.}$ , and the mass exposed in vacuo at from  $40^\circ$  to  $50^\circ \text{C.}$ , for the purpose of removing the water; or the original product may be dissolved in from 5 to 6 times its volume of petroleum ether of low boiling point, the greater part of the by-products remaining undissolved and the red-brown liquid organosol being dried with calcium chloride or dehydrated sodium sulfate. In this case a further part of the by-products separates along with the water. The petroleum ether is then distilled off from the liquid freed from the drying agent. The colloidal palladium oleate can be enriched in the "ointment" body by solution in petroleum ether and precipitation with alcohol. A product is thus obtained containing about 70 per cent of colloidal palladium oleate, which like the 25 per cent preparation, is absorbed as organosol by all organic substances dissolving wool fat. Instead of a palladium salt, a platinum or other salt of the platinum group can be used, for instance, the salt of divalent platinum resulting from the reduction of the platinum chloride-hydrochloric acid with sulfur dioxide. Wool fat impregnated with platinum salt, when acted on by an aqueous solution of potassium oleate, forms a colloidal platinum oleate  $(\text{C}_{18}\text{H}_{33}\text{O}_2)_2\text{Pt}$ . A mixture of the wool fat alcohols obtained from wool fat by saponification can be used in the same manner as wool fat. The wool fat alcohols are in their properties very similar to the wool fat itself and the mixture of alcohols obtained therefrom by saponification presents a still greater affinity for water than wool fat. The wool fat alcohols have a more solid consistency than the wool fat.\*

Meyer † reports an experiment on the hydrogenation of olive oil with a colloidal palladium hydroxide solution containing 0.2 gram

\* Amberger (*Kolloid-Zeit.* (1913), 13, 310) has prepared organosols of palladium, platinum, palladium hydroxide, palladium oleate and platinum hydroxide. In the preparation of the metallic organosols, hydrazine hydrate was used as a reducing agent. The palladium organosols (8 : 9 to 16 per cent Pd) had pronounced catalytic activity; small quantities dissolved in fatty oils were capable of transferring hydrogen to the unsaturated glycerides of the oil, with the formation of so-called hardened oils. The platinum organosols contained 8.14 to 18.4 per cent Pt. The hydroxide organosols were prepared by the interaction of the corresponding chlorides and sodium carbonate and the palladium oleate organosols from the chloride and potassium oleate in presence of wool fat. (*J. S. C. I.* (1914), 41.)

† Dissertation, Karlsruhe, 1912.

palladium and 0.34 gram gum arabic in 100 cc. Two volumes of olive oil to one volume of the colloidal solution were heated and agitated in an autoclave at a temperature of 70° to 80° C. under a hydrogen pressure of 6 atmospheres. Hydrogen was added to replace that absorbed. After one-half hour no further absorption of hydrogen could be noted, but the agitation was continued for 2 hours. The fat was then separated from the colloidal solution and boiled with water. A solid fatty product was obtained.

For the purpose of combining hydrogen with nitrogen to make ammonia the Badische Anilin & Soda Fabrik \* recommend cerium and a "promoter" as a catalytic agent.

With some exceptions, compounds of the alkali metals and the alkaline earth metals are said to act as promoters of the catalytic power. Also oxides of the rare earth metals, tantalum and niobium, as well as silica, may be employed as promoters. As a general rule those metals or compounds of the metals which yield oxides and salts which are non-reducible by hydrogen are suitable for use as promoters. On the other hand, the metalloids, such for instance as sulfur, selenium, tellurium, arsenic, phosphorus, and also the easily fusible and easily reducible metals, such for instance as lead, tin and zinc, generally act as contact poisons, whether the element be added or be present as such or in the form of a compound.

The following example is given. Take metallic cerium which has been prepared electrolytically and is in the condition of small grains, and mix it with about two per cent of its weight of powdered potassium nitrate, and then place the mixture in the contact tube. On passing a mixture of hydrogen and nitrogen through the tube, while heating, a catalytic agent is obtained which is said to give about three times the yield that the untreated cerium affords.

On account of the high price of osmium and ruthenium or their compounds they are used by the Badische Co.† for catalytic purposes on special carriers, in order to secure the greatest possible surface action. This is effected by solutions of their compounds such as alkali osmate and alkali ruthenate. The resulting contact masses can be employed either directly or after previous special treatment, such as heating, action of alkalies, acids, or reducing agents, etc. Asbestos, oxide of magnesium or aluminum, pumice stone, meerschäum, clay, cement, kieselguhr, metals, coal, etc., find application as carriers. For example, granulated meerschäum is saturated with a solution of potassium osmate in dilute potash lye, and the water evaporated in vacuo, so that 2 to 5 per cent of osmate remains upon the carrier.

In order to prevent the aggregation of a colloidal compound such as palladium hydrate and the like, it has been suggested ‡ to use a solid fat in which the colloidal particles are fixed so that the organosol is rendered stable. The use of a solid fat of low iodine number such as is prepared by hydrogenation and preferably one which has been completely saturated with hydrogen enables such metallic organosol, especially metal catalyzers, to be preserved over an indefinite period.

\* U. S. Patent 1,068,908, July 29, 1913.

† German Patent No. 292,242, December 22, 1912.

‡ Kalle & Co., German Patent No. 284,319, March 1, 1914. See also German Patents 268,811 and 289,620 Chem. Abs., 1916, 2618.

Colloidal palladium used by Albright\* in determining the hydrogen number of essential oils was a commercial product,† and the following is the manner of its preparation.‡

A solution of a palladium salt is added to a solution of an alkali salt of an acid of high molecular weight, in this case the sodium salt of protalbinic acid (an egg albumin decomposition product). An excess of alkali dissolves the precipitate formed and the solution is said to contain the palladium in the form of a hydrosol of its hydroxide. This solution is purified by dialysis and the hydroxide reduced with hydrazine hydrate. On further dialysis and evaporation to dryness there is obtained a water-soluble product consisting of colloidal palladium and sodium protalbinate in the form of black shining lamellae, which contains about 60 per cent palladium. The sodium protalbinate present in the mixture acts, when the material is in solution, as a "protective colloid."§

As is well known, colloids in general are precipitated, "flocked out," by ions<sup>+-</sup> (e.g.,  $As_2S_3$  by  $HCl$ ), due to a transfer of electrical charges, but in the presence of a protective colloid relatively large amounts of electrolytes are necessary to bring this about.

Hydrogenation involving the use of colloidal palladium differs from some other processes of catalytic reduction in that the reaction has not been observed to proceed in the absence of water nor if the proportion of water in the reaction mixture be too small. For instance, in the case of cottonseed oil, a portion of this material showed no absorption of hydrogen on being shaken with a small quantity of powdered colloidal palladium. The same result was obtained whether the oil was suspended in 95 per cent alcohol or dissolved in acetone. On adding 15 to 20 per cent of water to the acetone solution, however, reduction took place at a fairly rapid rate. If this more convenient form of colloidal palladium be not available, a substitute may be prepared as needed in the following way:|| 0.05 g. palladous chloride is placed in a shaking flask (see Fig. 50a, p. 306), followed by 50 cc. of 50 per cent alcohol and 1 or 2 cc. of a 1 per cent aqueous solution of gum arabic (the weight of gum used being about one-fourth the weight of the  $PdCl_2$ ). On shaking this mixture in an atmosphere of hydrogen, the chloride is reduced with formation of a black solution of colloidal palladium, which is rendered stable, i.e., "reversible," by the small quantity of the reversible colloid present, gum arabic. While this solution may be substituted for that of the technically prepared substance, it is actually more expensive, as experiments show that 0.02 g. colloidal palladium costing \$0.048 is at least as active as 0.05 g.  $PdCl_2$ , costing \$0.075. Paal's colloidal palladium and palladous chloride contain approximately equal percentages of the metal.

Certain substances are regarded as poisonous with respect to colloidal palladium, for example, formaldehyde contained in impure methyl alcohol is said to be harmful, and allyl isothiocyanate entirely inactivates it, so that mustard oil, for example, cannot be treated.

\* J. Am. Chem. Soc., 1914, 2188.

† Prepared by Kulle & Co., Biebrich am/R. Price about \$2.40 per gram. See Paal and Hartman, Ber., 43, 248-9, 1910.

‡ Paal and Amberger, Ber., 37, 124, 1904; Chem. Zentr., 1904, I, 572.

§ Paal and Amberger, loc. cit., see also Skita and Franek, Ber., 44, 2862, 1911; Chem. Zentr., 1911, II, 173.

|| Skita and Franek, loc. cit.

A catalyzer suitable for the hydrogenation and dehydrogenation of oils or other organic compounds, is prepared according to the **Badische Company**\* by treatment of an artificial zeolite such as sodium aluminum silicate with an acid solution of palladium chloride.†

**Fahrion** ‡ refers to the disadvantages of using so sensitive a catalyzer as palladium, especially in view of its high price (1 kilo palladium costs 6000 M.). According to Connstein the loss in palladium amounts to 5 to 7 per cent of the catalyzer employed, equivalent to 1.10 to 1.20 M. per 100 kilos fat. Bergius is reported by Fahrion as stating that the loss is about 1 g. of palladium per barrel of fat hydrogenated.

At the **Vereinigte Chem. Works** at Charlottenburg, hydrogenation is effected at 100° C., under a pressure of two to three atmospheres by means of 0.00002 part of palladium chloride in the presence of an alkali.§

The rate of hydrogenation is retarded in many cases by the presence of acids and Skita|| has obtained certain colloidal forms of the metals of the platinum group which are considered more suitable for the purpose than acid-liberating types.

A catalyzing device proposed by **Sabatier and Mailhe** ¶ consists of a network of wires, blades, rods, or tubes of catalytic materials adapted to be heated to the necessary temperatures by the passage of an electric current. Metals of the platinum or nickel series, or their alloys, or tantalum are suitable catalytic materials, or any metal coated with a catalytic metal may be used as the catalyzing material. Or the electrically heated metal network may be embedded in finely-powdered metal, or in metal oxide, carbonate, or other catalytic salt, suitable oxides being those of thorium, zirconium, uranium and titanium.\*\*

A catalyzer prepared by **de Montlaur** for the oxidation of ammonia, consists of a lustrous and adherent deposit of metallic platinum on such inert material as mica, glass or porcelain. It is obtained by coating the supporting surface with a solution of a platinum tetrachloride in an essential oil, preferably blue chamomile oil, and effecting reduction at a red heat, or by the decomposition at a bright red heat of sulphur compounds of platinum.††

**Neumann** proposes a support for contact material platinized only at the surface.‡‡ Porous supporting material is first subjected to a treatment by which an insoluble precipitate is formed in its pores. For example, it may be treated first with potassium silicate and then with hydrofluosilicic acid, or first with

\* British Patent No. 8,462, April 3, 1914.

† Cf. Mittasch, Schneider and Morawitz, following.

‡ Die Härtung der Fette, Braunschweig, 1915, p. 34.

§ Colletas, Les Matières Grasses, 1914, 7, 4151.

|| Seifen. Ztg., 1914, 1213.

¶ British Patent No. 2,011, February 8, 1915; Chem. Abs., 1916, 2032.

\*\* See French Patent No. 475,367, February 14, 1914; J. S. C. I., 1916, 32.

†† French Patent No. 445,857, September 15, 1911.

‡‡ German Patent No. 218,725, May 2, 1908; J. S. C. I., 1910, 487.

barium chloride and then with sulphuric acid. It is then washed, dried and platinized by heating and spraying with a platinum solution containing a reducing agent, after which, it is washed with water or with acids in which the precipitate is insoluble. By this method less platinum is used than by the process described in German Patent No. 188,503.\*

A contact substance for catalytic reactions described by **Niedenfuhr†** consists of a hollow perforated metal support coated with platinum electrolytically or otherwise.

Commenting on British Patent No. 18,642 to the Vereinigte Chemische Werke, **Fokin ‡** states that in 1906 he § published a communication on the reduction power of platinum hydroxide and, in fact, had made application for patent in Russia in April, 1909. In 1910 || he published a further communication in which the theory of the process and the function of the three factors, namely; the hydrogen atom, the hydroxyl group, and the double bond were discussed. Fokin observed that complex compounds of platinum were formed which are organosols. These possess a surface of "unlimited" area, which accelerate the reaction in the highest degree. Later in a publication on the preparation of isomers of oleic acid the procedure was more fully detailed by Fokin and methods of determining the hydrogen number were described, in which platinum oxide was used as the catalytic agent.¶

Galactose, resulting from protracted boiling of aqueous glue solutions, is advanced by **Classen \*\*** as a protective colloid for finely-divided metals, a salt of the metal being reduced in the presence of this agent.

The protective action of a number of colloids has been determined by **Groh ††** by measurements of the extent to which they retard the catalytic decomposition of hydrogen peroxide by colloidal platinum. The following values show the times required by colloidal platinum to effect 50 per cent decomposition of the peroxide without and in the presence of protective colloids. Without a protective colloid twenty minutes, 0.1 per cent gelatin two hundred and sixty-five minutes, 0.1 per cent gum arabic eighty-six minutes, 0.1 per cent dextrin sixty-six minutes, 0.01 per cent gelatin one hundred and fifty minutes, 0.01 per cent gum arabic thirty-nine minutes, 0.01 per cent dextrin twenty-eight minutes, 0.001 per cent gelatin one hundred and three minutes, 0.001 per cent gum arabic twenty-one minutes, 0.001 per cent dextrin twenty-three minutes, 0.0001 per cent gelatin seventy-one minutes.‡‡

**Zelinsky §§** has shown that catalytic dehydrogenation by palladium or platinum appears to be characteristic of hexamethylen hydrocarbons and may be used for the separation of pentamethylene and hexamethylene hydrocarbons and to the investigation of petroleum distillates. A mixture of methylcyclopentane and cyclohexane was subjected three times in succession to the action of platinum

\* J. S. C. I., 1908, 502.

† German Patent No. 225,705, July 31, 1908.

‡ Chem. Ztg., 1913, 61.

§ Journ. Russ. Phys. Chem. Gesell., 1906, 419 and Zeit. Electrochem, 12, 749.

|| Journal Russ. Phys. Chem. Gesell., 1910, 1074.

¶ Zeit. Analyt. Chemie, 48, 337, and Journ. Russ. Phys. Chem. Gesell., 1908, 700.

\*\* Zeitsch. angew. Chem. Referat., 1915, 58, German Patent No. 231,305, March 30, 1913.

†† Z. physik. Chem., 88, 414.

‡‡ Chem. Abs., 1915, 7.

§§ Ber., 1912, 3678; J. S. C. I., 1913, 76.



black at 300° C.; the quantity of hydrogen evolved was 93.4 per cent of the theoretical quantity calculated for the conversion of cyclohexane into benzene. The product was treated with sulphuric acid (2 vols. of acid of sp. gr. 1.84 mixed with 1 volume of fuming acid containing 7 per cent of anhydride), which sulphonated the benzene; the residual unattacked hydrocarbon, after distillation over sodium had the properties of the original pure methylcyclopentane. A fraction (boiling-point 102° to 104° C., sp. gr. 0.7647 at 18° C.), from Baku petroleum, after purification by treatment with sulphuric acid of the strength mentioned above, when treated in a similar manner yielded toluene and a hydrocarbon (boiling-point 101° to 102.5° C. sp. gr. 0.7488 at 20°/4° C.) which was probably a derivative of cyclopentane or cyclobutane. A petroleum fraction (boiling-point 100° to 100.5° C.) obtained by repeated treatment of so-called "naphtha-heptanaphthene" with a mixture of nitric and sulphuric acids, gave similar results.

**Normann and Schick** hold that, contrary to the views of **Lehmann**, osmium metal and not the dioxide, is responsible for the catalytic action noted in fat hardening.\*

Colloidal hydroxides of osmium and ruthenium and the colloidal metals themselves may be prepared according to **Kalle und Co. A. G.**† by means of a protective colloid. The tetroxide of osmium or of ruthenium is mixed with the protective colloid, such as sodium protalbinat or lysalbinat, and with alcohol, and the mixture evaporated carefully to dryness. The solid colloidal hydroxide thus obtained may be reduced to the colloidal metal by means of hydrogen at a low temperature. The advantage of this modification is found in avoiding the admixture of salts and alkalies and in the fact that dialysis is not necessary. The preparation in detail is as follows:

One part sodium protalbinat is dissolved in 200 to 300 parts water and then 1.34 parts osmium tetroxide in about 60 volumes cold alcohol is added. The mixture is then either evaporated to dryness in vacuo, or else gently heated on the water-bath to remove most of the solvent and finally dried in vacuo. The osmium tetroxide is reduced by the alcohol to the tetrahydroxide  $\text{Os}(\text{OH})_4$ . If evaporation is effected in pleno, ammonia must be added from time to time in order to prevent reoxidation of the hydroxide to the volatile oxide. If the process is applied to ruthenium tetroxide, the alcohol must be added to the solution of the protalbinat or lysalbinat of sodium, and the tetroxide, dissolved in water is allowed to flow gradually in the solution with stirring. Ruthenium chloride,  $\text{Ru}_2\text{Cl}_6$ , or the potassium salt of the acid may be used as the initial material, which is first converted by treatment in a current of chlorine, in the presence of water with heating, into the tetroxide. If the osmium or ruthenium hydroxides are to be converted into the corresponding colloidal metals, the solid products are carefully powdered and treated in a tube freed from air by carbon dioxide with hydrogen at 30° to 40°, obtaining thereby colloidal Os or Ru. If the colloidal tetrahydroxides are to be obtained in dilute aqueous solution, a smaller amount of stabilizer will be sufficient.‡

\* Seifen. Ztg., 1914, 1111; Arch. Pharm., 1914.

† German Patent No. 280,365, July 30, 1913. Addition to German Patent No. 248,525; J. S. C. I., 1915, 492 and 1912, 952.

‡ Chem. Abs., 1915, 1378; Zeitsch. angew. Chem., Referat, 1915, 22.

Osmium and ruthenium compounds are used as catalyzers in the synthesis of ammonia. Asbestos, meerschäum, or similar material is soaked in a solution of alkali osmate, or alkali ruthenate, and dried. The contact mass thus obtained can be employed for catalytic purposes either directly, or after being heated, or acted upon with acid or reducing agents.\* Osmium as an oxidizing catalyst is described by Hofmann.† Ruthenium is favored by Mittasch as a hydrogenating catalyzer.‡

By supporting platinum on charcoal, a catalyzer is obtained, according to Mannich,§ which is free from the disadvantages of colloidal platinum and is more efficient than the metal on an indifferent carrier. Purified animal charcoal is recommended. A platinum black charcoal catalyzer has been found to absorb great quantities of hydrogen. The results obtained on castor and peanut oils show distinctly advantageous results. Palladium supported on small pieces of coke is used as a catalyzer by Verona-Rinati.||

Platinum and carbon, especially charcoal, in admixture, have been found by Ellis to afford a desirable catalytic agent.¶ In preparing the catalyzer, care is taken to exclude oxygen. The cerium group of metals as hydrogen carriers is considered by Ellis,\*\* who recommends cerium incorporated with charcoal.

By the addition of animal charcoal Mannich and Thiele †† find the absorption capacity of palladium for hydrogen is greatly increased, and the mixture absorbs much more gas than the total quantity absorbed by the separate constituents. A catalyst which rapidly effects the complete hydrogenation of fats is prepared by shaking powdered, ignited animal charcoal with palladium chloride (preferably 2 per cent) solution and hydrogen until no more gas is absorbed. The powder is then washed and dried and can be kept unaltered. It can be used in conjunction with any solvent and, after hydrogenation, is completely separated by simple filtration, without leaving any trace of metal in the fat. In these respects it is superior to colloidal palladium preparations.

An oil such as peanut oil can be hydrogenated by means of  $\frac{1}{100}$  of its weight of animal charcoal containing 0.2 per cent palladium (ratio of metal to oil = 1:30,000) into a tallow-like mass, with M.P. 51° C. and iodine value 45.5.

\* Badische Co., British Patent No. 12,977, June 4, 1913.

† British Patent No. 20,593, September 11, 1913; Chem. Abs., 1915, 697.

‡ U. S. Patent No. 1,173,532, February 29, 1916.

§ Seifen. Ztg., 1914, 1174.

|| Annali Chim. Appl., 1914, 99.

¶ U. S. Patent No. 1,174,245, Mar. 7, 1916.

\*\* U. S. Patent No. 1,167,280, Jan. 4, 1916.

†† Ber. Deutschen Pharm. Ges., 1916, 26, 36-48; J. S. C. I., 1916, 548.

Even by the use of 1 part of palladium (distributed over animal charcoal) to 150,000 parts of peanut oil the hardening can be effected in one operation.

A catalyzer used in the production of propylene by the union of acetylene and methane and containing two catalytic metals is prepared by Heinemann \* in the following manner:

One of the contact metals, for example, copper, is deposited in a porous body, for example, pumice stone, either electrolytically, or by the reduction of a copper salt. The pumice stone, provided with a coating of copper, or having its pores partly filled with copper, is then dipped in a solution of a salt of a contact metal of the platinum class, for instance, chloride of platinum, and is dried. The salt is then reduced. In this way there is obtained a contact body consisting of two metals which are stated to exert a mutual balancing effect on one another, the more active property of the platinum group metal being mitigated by the less active property of the other metal associated therewith, and allowing the desired reaction to take place at a moderate temperature.

Böeseken and Hofstede† carried out experiments on the absorption of hydrogen by cinnamic acid and its esters, using a palladium solution prepared according to the method of Skita and Meyer and found considerable irregularity in the velocity of the reaction under what were thought to be comparable conditions. The presence of small amounts of oxygen in the hydrogen was found to exert a marked activation of the catalyzer. It is concluded that even in this apparently simple catalytic reduction, viz., an irreversible reaction with elementary catalyzer, the phenomena are far more complicated than could be expected.

An interesting form of catalyzer investigated by Mittasch, Schneider and Morawitz‡ contains the elements of a metal of the platinum group and an aluminate silicate, and can be obtained by taking an aluminate silicate containing water, such as a natural or artificial zeolite, and replacing a part or the whole of its content of alkali metal or alkaline earth metal, by the platinum metal.

The product obtained can be subjected to further treatment. For instance, it may be heated and reduced, and this reduction is desirable if the catalytic agent is to be employed for the hydrogenation of organic compounds. After such reduction, the catalytic agent contains a platinum metal in a metallic form and also the elements of an aluminate silicate.

The introduction of the platinum metal into the silicate can be effected by digesting the alkali metal aluminate silicate with a solution of a platinum metal salt. Or, the zeolite as obtained (or after being gently heated, so that some of the water is driven off) may be soaked in a solution of a platinum metal salt,

\* U. S. Patent No. 1,202,385, October 22, 1916.

† Proc. Akad. Wetensch., Amsterdam, 1918, 20, 424; Chem. Abs., 1918, 1144; J. S. C. I., 1918, 136A.

‡ U. S. Patent No. 1,215,396, February 13, 1917. See also British Patent 1,358, Jan. 27, 1915.

so that the platinum metal salt enters the zeolite, and some replacement of the alkali metal or alkaline earth metal by a platinum metal takes place, although the alkali remains in the mass.

*Example:* Digest 100 parts of the artificial zeolite, sodium aluminate silicate such as the ordinary commercial granular sodium permutite found on the market) with a weak hydrochloric acid solution containing one-tenth of a part, to half a part, of palladium subchloride, either at ordinary temperature, or while warming, until the solution is decolorized. If the catalytic agent is to be used for hydrogenation purposes, wash the mass well and dry it and reduce with hydrogen at from 150° to 200° C., or with formaldehyde at a lower temperature. The catalytic agent which is obtained can be used (either directly, or after pulverization) for the hydrogenation or dehydrogenation of organic compounds, and, when liquids are treated, these can with advantage be allowed to trickle over the catalytic agent. Instead of sodium permutite, other aluminate silicates containing an easily replaceable base, or more than one easily replaceable base, can be employed, for instance, natural zeolites can be used, such as analcime, natrolite, chabasite. In a similar manner, other platinum metal zeolites can be prepared, for instance, those of platinum itself and of rhodium, iridium, ruthenium and osmium. A platinum zeolite can be obtained by heating an artificial zeolite until more or less of the water has been driven off, and then soaking it in a solution of platinum hydrochloride, drying and heating, whereupon, any soluble salts, such as sodium chloride can be removed by washing or digesting. An osmium zeolite can be prepared by soaking a zeolite in a solution of potassium osmate, and heating. The artificial or natural zeolite can first be converted into ammonium zeolite, and this either directly or after heating can be converted into osmium zeolite, by treatment with potassium osmate.\*

Amberger † states that practically all previous preparations of colloidal osmium have resulted in a colloidal oxide or hydroxide. Amberger has prepared organosols of platinum and palladium in wool fat and now applies the same principle to the preparation of colloidal osmium.

Two parts of osmium tetroxide are dissolved in 7 parts dilute caustic soda and alcohol added till sodium osmate is formed. This is gradually stirred into 13 parts of warm wool fat, intimately mixed, then hydrazine hydrate is added slowly; the emulsion swells and takes on a metallic grey color and on standing twenty-four hours becomes black. Another warming and the addition of more hydrazine hydrate are necessary for complete reduction. To remove by-products the mass may be dissolved in petroleum ether, washed, dried and the ether distilled off. There results a brown-black salve, easily soluble in organic liquids which dissolve wool fat, giving transparent, brownish black liquids. For analysis this salve is dissolved in petroleum ether, precipitated by more than an equal volume of alcohol and osmium determined in the dry precipitate by the method

\* Artificial zeolites are put on the market under the names of permutite, and are described in British Patent No. 23,706/12 and also in the article "On Artificial Zeolites" by Siedler, on page 262 of the report of Section 2 of the Seventh International Congress of Applied Chemistry held in London in 1909.

† Kolloid-Z., 17, 47-51, 1915; Chem. Abs., 1915, 3159.

of Knotte.\* The osmium content is about 7.9 per cent. This contains oxides of osmium as well as metallic osmium. In order to reduce the colloidal oxides the original emulsion, after reduction with hydrazine hydrate, is dissolved in petroleum ether and precipitated by alcohol; nearly all the osmium precipitates in combination with a large proportion of the wool fat. This coagulum is washed free from alkali, dried, powdered and then reduced with dry hydrogen first in the cold then at 30° to 50°. This gives a stable organosol, easily soluble in liquids which dissolve wool fat. The osmium content is 20.9 per cent. If instead of reducing the sodium osmate wool fat emulsion with hydrazine hydrate, sulphuric acid is added, an organosol of osmium dioxide is formed, one preparation of which gave 0.53 per cent osmium dioxide. By dissolving in petroleum ether and precipitating with alcohol, then washing, the concentration may be raised to an osmium dioxide content of 24.5 per cent.

Silicic acid is used by Schwerin,† to form stable colloidal solutions of metals' for example, a solution of silicic acid containing about 2.5 per cent of the acid is mixed with a diluted solution of a gold or silver salt and the metal is reduced by a reducing agent suitable for separating it in the colloidal form. If, for instance, hydrazine hydrate is the reducing agent a completely clear brown silver sol, or deep blue gold sol, is obtained.

By the method of Schwarzman‡ a precipitated sesquioxide is treated with a soluble salt of a platinum group metal, such as palladium, until a certain amount of active compound is deposited; the treated sesquioxide is then dried at a comparatively low temperature, best after thorough washing; the hydrated sesquioxide being advantageously formed under conditions permitting adsorption or absorption of colloid organic matter, such as keratin dissolved in caustic alkali.

The sesquioxide may be ferric hydrate, chromium hydrate or aluminum hydrate, the latter giving best results. Other hydrated non-basic or slightly acid oxides, such as hydrated tin oxide, titanate acid, tungstic acid, etc., may be used but have no particular advantage over the sesquioxides. Hydrated oxides of the type of cobalt oxide, nickel oxide and zinc oxide, for general hydrogenation work are stated to be far inferior to the sesquioxides. Palladium is the best metal of the platinum group to use for the purpose of hydrogenating, although platinum compounds may be used for this purpose, and for oxidizing are even better. Osmium, ruthenium, and rhodium also may be used.

The hydrated sesquioxides although not active as hydrogenating agents *per se*, according to Schwarzman appear to heighten the activity of palladium in some degree as "cocatalysts." This is said to be particularly true with palladium hydroxide distributed through hydrated alumina. Anhydrous alumina, as a carrier, he states affects the activity of palladium but little if at all. The hydrated oxides are all readily soluble in dilute acids, which is convenient in regenerating the catalyst.

\* Z. angew. Chem., 15, 393, 1902.

† U. S. Patent No. 1,119,647, December 1, 1914.

‡ U. S. Patent No. 1,111,502, September 22, 1914.

According to a formula by Schwareman, 342 parts of aluminum sulphate,  $\text{Al}_2(\text{SO}_4)_3$ , are dissolved in 3400 parts of water and the temperature is adjusted to about  $170^\circ \text{F}$ . A solution of 240 parts of commercial caustic soda or the equivalent amount of carbonate, in 1000 parts of water at about the same temperature, is then added. The addition of soda results in the precipitation of hydrated alumina. This precipitate is washed until all the soluble salts have been removed. The hydrate so obtained is next treated to incorporate palladium. For this purpose 0.312 part of palladium chloride are dissolved in 100 parts of water and the hydrated alumina treated with this solution. The mixture then is brought to a boil, filtered and the solid material washed. This treatment leaves the alumina charged with merely the quantity of palladium it will absorb. The material after washing is dried at a moderate temperature. A high temperature is apt to cause dehydration of the palladium oxide, and of the alumina as well, to an undesirable extent. A drying temperature of about  $170^\circ$  is best. Using the amounts of materials indicated, there will be obtained about 156 parts of a fine-grained brown powder containing approximately 0.2 per cent palladium. Generally most of this palladium exists in the catalyst in the form of a hydrate.

A more active catalyst in a somewhat different physical form is obtained by using a little keratin or other organic colloid dissolved in the caustic soda used for forming the hydrated alumina. Wool is very well suited. The same reagents in the same proportions may be used together in the manner indicated above with the exception, that about 5 parts of wool, are previously dissolved in the caustic soda solution. The final material obtained is more fluffy and bulky than where the wool is omitted. This fluffy bulky catalyst is kept in suspension in the oil with particular readiness.

Schwareman states that since palladium oxide does not form soaps with fatty acids, it may be employed in hydrogenating free oily and fatty acids and that as alumina is insoluble in fatty acids, the palladium carried by this sesquioxide makes a particularly good catalyst for this purpose.

Sulzberger\* considers that the most efficient way of intimately distributing a catalyzer is by dissolving the initial catalytic material in the body, which is to be treated, and then, should not the form, in which the material was dissolved in the body, be *per se* catalytically active, transforming it by chemical reaction or otherwise into a product of catalytical efficiency.

As an example, he cites the hardening of cottonseed oil with a catalytic agent belonging to the platinum group: palladium. Sulzberger notes that a palladium product of the desired quality can be obtained by treating a palladium salt, as for instance, "palladium-ammonium chloride" with sodium oleate, which resulting compound is soluble in cottonseed oil and can be used as a catalyzer of highest efficiency, as, being so finely-divided in the oil, even very small quantities will give good results. The solution of this product in the oil darkens when heated, in consequence of its palladium content and such solution hardens to a product of jelly-like consistency at certain temperatures and when containing certain amounts of the palladium body. Cottonseed oil, when containing this body is readily hardened when treated with hydrogen.

\* U. S. Patent No. 1,171,902, February 15, 1916.

In cases where the product, which is to act as a catalyzer, cannot be made use of in a form soluble in the body which is to be treated catalytically, the very fine distribution of the catalytic agent may be accomplished by dissolving it in a solvent, which mixes with the body to be treated, with or without precipitation. For example, the above palladium compound being soluble in ether, could be added to the cottonseed oil in such solvent.

**Killing**\* employs a composition of thorium oxide and a metal of the platinum group in a state of very fine division as a catalyst in a gas igniting device. In producing this material nitrate of thorium and chloride of platinum, are mixed, afterward ashing or burning out the mixture, producing a fixed sponge of thorium oxide and platinum black. The proportions which Killing has found best suited to the end in view are 1 part of thorium nitrate to 2 to 2½ parts of platinum black. Iridium and other metals of the platinum group may be substituted for platinum or mixed therewith without destroying the efficiency of the compound. Other rare earths may be substituted for the thorium, as, for instance, cerium, and zirconium.

The effect of the hydroxides or oxides of iron, copper, mercury and zinc on the catalytic activity of palladium hydrosol has been studied by **Paal** and **Hartmann**.† Ferrie hydroxide has no action while copper hydroxide lowers the activity. Zinc hydroxide at first depresses the activity but after a time the catalyst becomes more than normally active. Yellow mercuric oxide permanently impairs the activity of the hydrosol.

Users of platinum in catalytic reductions have begun to recognize that it sometimes matters whether the catalyst is entirely free from occluded oxygen at the outset or has been freely exposed to the air. For example, **Hess**‡ has shown that the rigid exclusion of oxygen is necessary in order to insure success in the reduction of pyrrole and some of its derivatives. **Willstatter** and **Jaquet**§ describes cases of the opposite kind, in which the catalyst must be activated by exposing it to oxygen at intervals. The most interesting example is phthalic anhydride. If this is dissolved in glacial acetic acid and treated with hydrogen in the presence of platinum-black, only a small volume of gas is absorbed, unless the apparatus is opened as occasion requires and the catalyst is agitated in contact with the air. Then the reduction proceeds smoothly to hexahydrophthalic acid. It appears, therefore, that platinum and oxygenated platinum must be regarded as distinct catalysts. (See page 260.)

\* U. S. Patent No. 614,557, Nov. 22, 1898.

† Ber. 1918, 51, 894 and 711; J. S. C. I., 1918, 560A, 579A.

‡ Ber. 1913, 46, 3120, 4104.

§ Ber. 1918, 51, 707; J. S. C. I., 1918, 560A; J. Chem. Soc., 1918, i, 391.

## CHAPTER XI

### THE OCCLUSION OF HYDROGEN AND THE MECHANISM OF HYDROGEN ADDITION

As an acquaintance with the subject of hydrogen addition and reduction by hydrogen of various bodies may lead to a broader knowledge of catalytic reactions in the hydrogenation of oils, the following notes by various observers are included.

Sieverts and Krumhaar\* did not find hydrogen to be absorbed by the metals cadmium, thallium, zinc, lead, bismuth, tin, antimony, silver and gold. The solubility in copper, nickel, iron and palladium is shown in the graphic curve diagram. (Fig. 50.)

The curves show that the solubility increased regularly with the temperature up to the melting point and then suddenly increased, the solubility in the liquid metal then increasing regularly in the same manner. With palladium, however, the solubility was independent of the temperature up to the melting point and then diminished to one-half, and in the liquid metal was again independent of the temperature. On cooling, copper retained 20 per cent and nickel 8 per cent of the hydrogen absorbed, and in the case of iron, the evolution of gas was so violent on solidification that the tube was blown to pieces, leaving a spongy regulus. In experiments with alloys it was found that the addition of gold lowered the solubility of oxygen in silver. The copper alloys and hydrogen formed three groups: (a) those in which the solubility was not influenced, such as silver; (b) those in which the solubility was lowered, such as gold, tin, aluminium; (c) those in which the solubility was higher than that accounted for by the copper content, such as nickel and platinum. The solubility in copper alloys was proportional to the square root of the pressure, and the view that occlusion was due to adsorption is untenable, and although Sieverts and Krumhaar hold the view that adsorption did not exist at high temperatures, they do not express any opinion about low temperature conditions, and they put forward the view that gases and metals form solid and liquid alloys, the solubility of which does not follow Henry's law, but is expressed by the formula  $\frac{\sqrt{P}}{m}$ .

Exhaustive data are given by Sieverts (Z. physik. Chem. (1911), 591) of the solubilities of hydrogen in the three metals, copper, iron and nickel, at pressures up to 1.5 atmospheres, and temperatures from 400° to 1600° C. It is shown in the case of nickel that the amount of gas absorbed by the metal under given conditions of temperature and pressure is independent of the amount of metallic surface. The hydrogen-containing metals are therefore true solutions. At constant temperature the solubility both in solid and liquid metals is proportional to the square root of the gas pressure, the quotient  $\frac{\sqrt{P}}{m}$  (where  $m$  is the mass of gas absorbed by 100 grams

\* Berichte (1910), 43, 893.



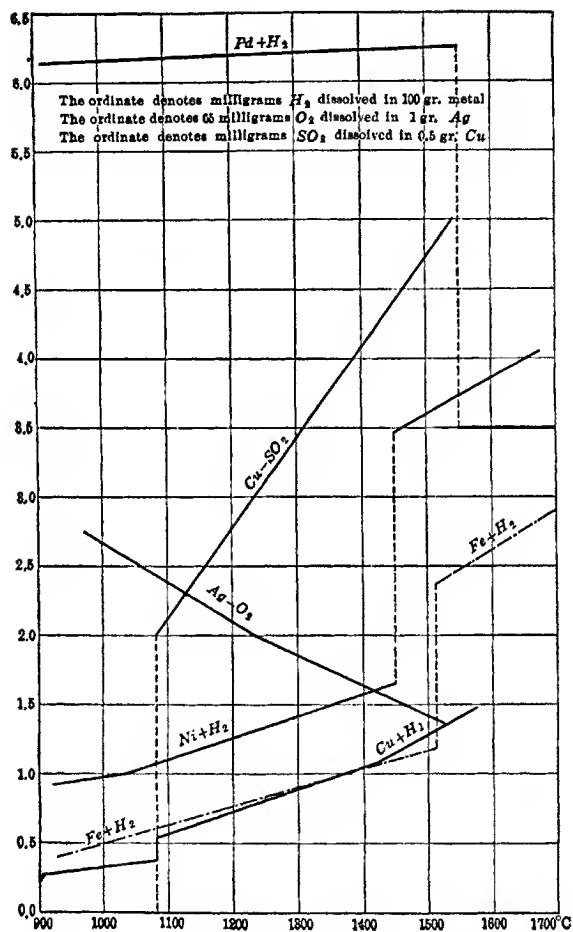


FIG. 50.

of metal) being remarkably constant for values of  $p$  above 10 mm. At constant pressure the solubility increases with temperature, and shows a sudden increase at the melting points of all three metals. The transition from  $\beta$  to  $\gamma$  iron is also marked by a rapid increase in solubility between 850° and 900° C. This discontinuity though very marked is not so sudden as that at the melting point. The transition from  $\alpha$  to  $\beta$  iron is not accompanied by any change in solubility. In the liquid metals the solubility continues to increase with rise of temperature, probably more rapidly than in the solid state. On solidifying in an atmosphere of hydrogen all three metals "spit." Copper gives off about twice its volume of hydrogen (at 1084° C. and 760 mm.) iron about 7 times its volume (at 1510° C. and 760 mm.) and nickel about 12 times its volume (at 1450° C. and 760 mm.). The regulus contains cavities in which hydrogen may be retained. It is only, however, after very rapid cooling that any considerable quantity of the absorbed hydrogen can be retained at ordinary temperatures.

With regard to the occlusion of hydrogen by various metals, the following table is instructive.\* The numbers indicate the volumes of hydrogen under normal conditions absorbed by one volume of the metal.

Silver wire.....	0.21
Silver powder.....	0.91-0.95
Sheet aluminum.....	1.1-2.7
Reduced cobalt.....	59-153
Copper wire.....	0.3
Reduced copper.....	0.6-4.8
Iron wire.....	0.46
Cast iron.....	0.57-0.8
Reduced iron.....	9.4-19.2
Magnesium.....	1.4
Reduced nickel.....	17-18
Gold leaf.....	0.48
Precipitated gold.....	37-46
Molten lead.....	0.11-0.15
Zinc.....	Traces

From a study of the action of nickel and hydrogen on various hydrocarbons at different temperatures, the following conclusions are drawn by Padoa and Fabris†: (1) In the dehydrogenation of monocyclic and polycyclic hydrogenized hydrocarbons, gaseous hydrocarbons are formed to some extent. If a hydrocarbon yields several hydrogenation products, the most highly hydrogenized one is most readily decomposed in this manner. Of the hydrocarbons examined, tetra- and di-hydrophenanthrene yielded no hydrocarbon decomposition

\* Abegg and Auerbach, Hdb. d. Anorganischen Chemie Vol. II, part I, 55.

† J. S. C. I. (1908), 1083.

products even under increased pressure, and tetrahydronaphthalene did not under atmospheric pressure.

(2) The decomposing action of nickel is influenced by pressure.

For instance, at atmospheric pressure, tetrahydronaphthalene is simply dehydrogenized with liberation of hydrogen, whereas under a pressure of 3 atmospheres, gaseous hydrocarbons are formed. (3) The several hydrogenation products of a hydrocarbon can each be obtained from the most highly hydrogenized product by the action of nickel at a definite temperature, but it is not possible to effect a gradual progressive splitting off of hydrogen. In almost all cases dehydrogenation begins at a higher temperature than hydrogenation. Under atmospheric pressure hydrogenation and dehydrogenation are distinct processes; in most cases nickel can effect either reaction, but on certain compounds, the nickel acts only in one way. Under increased pressure, the two limits of temperature, viz., the highest at which hydrogenation is possible and the lowest at which dehydrogenation takes place, are closer together, and under certain conditions, the two processes may proceed simultaneously until equilibrium is attained.

Relative to its behavior to hydrogen, Holt, Edgar and Firth \* state that palladium may exist either in an active or a passive state, the former rapidly taking up hydrogen, the latter being practically inert. Heating to a temperature of 400 degrees in hydrogen and cooling renders the palladium very active. New palladium may be made active by the repeated oxidation and reduction of the surface. The activity diminishes gradually on standing, but may be restored on heating.

When spongy palladium was exposed to hydrogen at temperatures from  $-50^{\circ}\text{C}$ . upwards, Guthrie (Ber. (1913), 1453) found that the amount of occluded gas steadily decreased from  $-50^{\circ}\text{C}$ . (917 volumes to 1 of palladium) to a minimum at  $20^{\circ}\text{C}$ . (661 : 1) then slowly rose to  $105^{\circ}\text{C}$ . (754 : 1). The hydrogenized palladium was pyrophoric.

It is suggested that the activity is due to the presence of a metastable modification of the palladium which gradually reverts to a more stable variety at ordinary temperature. Measurements have been made of the rate of sorption (this term includes both adsorption and absorption) of hydrogen by palladium free from hydrogen, and palladium containing varying amounts of previously-sorbed hydrogen. No marked difference was observed between the action of moist and dry hydrogen. With palladium containing little or no hydrogen the rate of sorption first increases rapidly and then slowly diminishes. On the other hand, if the palladium has already sorbed considerable quantities of hydrogen the initial increase is not observed. It would appear that when active palladium is exposed to an atmosphere of hydrogen there is first a rapid condensation (adsorption) of the gas at the surface, probably in the form of complex molecules, forming a layer of high vapor pressure. This is

\* Z. physik. Chem., 82, 513.

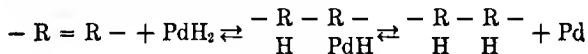
followed by a slow diffusion (absorption) into the interior of the metal. This would explain the rapid rise in pressure followed by slow increase observed when palladium partially saturated with hydrogen is exposed to a vacuum. The sorption is accompanied by evolution of heat. Measurements were also made of the rate of diffusion of hydrogen through a palladium tube. The rate is found to increase with rise in temperature, but it is also influenced by the state of the metal. This accounts for the fact that the same diffusion velocity is not always found at the same temperature. It is very doubtful that the hydrogen sorbed by the palladium is at the same concentration throughout the metal, even after long standing.

The rate of absorption of hydrogen by limonene in the presence of platinum black has been studied by Vavon (Comp. rend. (1914), 158, 410), and two stages or phases of the reaction were noted. The velocity curves for the absorption of hydrogen have a gradient which varies considerably with the quantity of catalyst present. Apparently the metal can become fatigued so that while it is active enough to bring about the easier stages of hydrogen addition, it is not powerful enough to effect the more difficult stages of saturation. This is more marked after the catalyst has been heated to a temperature of 300° C. or higher, when the activity can be varied and suited to bring about hydrogenation in a selective and regular manner. When heated above 500° C. platinum black is transformed into an inactive modification.

The work of Andrew and Holt (Proc. Roy. Soc. (1913), A, 89, 170), which leads to the conclusion that palladium is dimorphic, is discussed by Halla (Z. physik. Chem. (1914), 86, 496), who shows that palladium black prepared by Graham's method is not inactive. He also shows that occlusion by active palladium is not hindered at ordinary temperatures by contact with the inactive metal.

Mixtures of hydrogen and oxygen combine with explosion on contact with platinum or carbon which has been heated to a temperature sufficient to cause the emission of electrically-charged particles from the surfaces of platinum or carbon. If platinum is exposed to Roentgen rays which cause the emission of charged particles an explosion may be brought about without heating the platinum. (J. R. Thompson, Chem. Ztg., Rep. (1914), 15.)

Investigations directed towards an explanation of the precise nature of hydrogen transfer by means of the platinum metals are not lacking. Wieland\* assumes that palladium hydride, or for that matter any metal hydride, unites as such with the unsaturated compound at the double bond and that the labile addition product breaks down, with retention of the hydrogen and elimination of palladium, the latter being then in condition to take up additional hydrogen and again form an addition product. From a thermodynamic standpoint the hydrogenation process appears to be a reversible reaction. In the case of ethylene compounds, and in fact, in general, the reaction is exothermic, but is endothermic in the case of the double bonding of the aromatic series. Thus the metal addition product would appear in the reaction equilibrium as follows:



\* Ber., 45, 484.

In this connection it may be stated that Skita and associates have isolated an addition product of palladium chloride with an unsaturated body but work along this line has not been extensive and the explanation advanced that catalyzers simply split the hydrogen molecule to yield hydrogen in an atomic or nascent condition is for the present perhaps as satisfactory as any.\*

Troost and Hautefeuille† believed that their experiments vindicated the formation of a definite compound  $\text{Pd}_2\text{H}$ , while Dewar‡ suggested the existence of  $\text{Pd}_3\text{H}_2$ . The experiments of Hoitsema§ indicate that between 20 and 200 degrees no definite compounds of palladium and hydrogen exist.

**Sabatier**|| considers nickel catalysis to be due to the formation of hydrides. First hydrogen acts on the metal, quickly forming a compound in the superficial layers of the latter. The hydride which results becomes decomposed, and in the presence of bodies which are capable of hydrogen addition, union with the hydrogen takes place. The metal is regenerated and the rôle endlessly repeated.

The variations in activity of nickel which have been noted probably depend on the formation of different hydrides. Thus, for example, well-prepared nickel catalyzer may form the perhydride  $\text{NiH}_2$  which is sufficiently active to hydrogenate benzol. Nickel prepared at high temperatures, or if slightly poisoned, may form the lower hydride  $\text{NiH}$

|| which is not active on benzol but which is catalytic for olefines  $\text{NiH}$  and nitro compounds.

Were this assumption correct it would appear as a consequence that nickel and the other active metals (copper, iron, cobalt and platinum) not only should effect a union of hydrogen, but also that hydrogen-containing compounds should suffer removal of their combined hydro-

\* Some experimental work of Paal (Ber., 45, 2221) is of interest. Paal notes that apparently only those compounds with two C : C groups in which these groups are separated by at least one carbon atom can be catalytically reduced stepwise. Thus  $\text{PhCH} : \text{CHCH} : \text{CHAc}$  in alcohol with colloidal palladium and two hydrogen equivalents give about 50 per cent each of the original ketone and of the fully reduced compound ( $\text{PhCH}_2$ ) Ac. Similar results were obtained with  $\text{PhCH} : \text{CHCH} : \text{C}(\text{CO}_2\text{H})_2$ , piperinic acid and piperine. Phorone, on the other hand, yields almost quantitatively dihydrophorone,  $\text{Me}_2\text{CHCH}_2\text{COCH} : \text{CMe}_2$ , b. 176 degrees; semicarbazone, needles, m. p. 133 to 134 degrees. (Chem. Abs.)

† Comp. rend., (1874), 78, 686.

‡ Chem. News, (1897), 76, 274.

§ Zeit. phy. Chemie (1895), 1.

|| Die Hydrierung durch Katalyse, Leipsic (1913), 17.

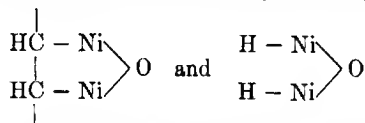
gen, the metals acting as dehydrogenating catalyzers. This actually proves to be the case. Between 250° to 300° C. finely-divided copper readily acts as a dehydrogenating catalyst, converting primary alcohols to aldehydes and secondary alcohols to ketones, in fact affording a very advantageous method for bringing about these transformations.

*Results obtained by hydrogenation with nickel.* The results obtained by hydrogenation with reduced nickel are classed by Sabatier into 4 groups:

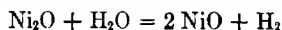
1. Simple reduction without the fixation of hydrogen.
2. Reduction effected simultaneously with the fixation of hydrogen.
3. Fixation of hydrogen by addition to the molecules where multiple bonds exist.
4. Hydrogenation effected with the decomposition of the molecule.

The well-established impossibility of effecting all these changes with any metal leads Sabatier to think that for nickel there exists many degrees of combination with hydrogen. Nickel obtained by the reduction of the chloride, as well as that reduced at a temperature above 400° C. is, without doubt, able to produce only a primary hydride, analogous to that of copper and capable of acting on nitro groups or on the double ethylene bond. Only "healthy" nickel, such as that produced by the reduction at a low temperature of the oxide obtained from the nitrate, is able to form a perhydride capable of hydrogenating the aromatic ring.

In the case of nickel oxide catalyzers Erdmann indicates that the transference of hydrogen probably takes place in one of two ways: either an intermediate phase represented by the compounds



or a decomposition of water may take place in accordance with the reaction:



yielding hydrogen in a nascent state which is assumed to unite with the unsaturated fat while the nickel oxide formed is reduced to the suboxide by hydrogen in the molecular condition.

In an experiment conducted by **Mayer** and **Altmayer\*** nickel, reduced from the oxide by hydrogen, was introduced into a Jena glass vessel in an electric furnace, and after complete exhaustion, known

\* Berichte (1908), 41, 3062.

quantities of hydrogen were introduced, and the temperature kept constant until absorption ceased. The amount absorbed, at temperatures of 360° to 560° C., was at each temperature proportional to the pressure of the hydrogen. At 360° C. 1 volume of nickel absorbed 50.5 volumes of hydrogen at a pressure of 300 mm., whilst at 560° C. the same absorption occurred when the pressure was raised to 440 mm. Within the experimental limits, then, the system nickel-hydrogen is bivariant, the volume absorbed being dependent both on temperature and on pressure.

Amorphous palladium absorbs hydrogen far more rapidly than the crystalline form, but holds it only feebly. The amorphous form also takes up hydrogen and transmits it to the crystalline variety, so that crystalline palladium coated with the amorphous metal will absorb hydrogen much more rapidly than when uncoated.\*

Adsorption is quite variously regarded by various authorities as one of the following: (1) True chemical combination. (2) True solid solution. (3) A modified solid solution in which practically only the outer layers become saturated owing to the difficulty of diffusion in solids. (4) Condensation on the outside of the surface of the solid. According to **McBain**† the first three are contrary to the requirements of thermodynamic theory, and the fundamental assumption of the third is disproved by experiments involving the time required for adsorption of hydrogen. The fourth is found insufficient to explain the somewhat complex time relationships studied here, which, however, point strikingly to the conclusion that both true solid solution (true diffusion) and surface condensation occur. They are independent of each other and their relative importance and magnitude depend upon the conditions of the experiment.

The non-committal name "sorption" is coined to designate the sum total of the phenomena, while "absorption" and "adsorption" are restricted to the dissolved and superficially-condensed matter respectively. It is found that the surface condensation requires only a few minutes for completion, whereas absorption requires, in the case of hydrogen diffusing into carbon at the temperature of liquid air, a dozen hours for practical completion. Thus it was possible to isolate the two phenomena and to study them more or less independently of each other. For instance, by suitable manipulation a sample of carbon can be prepared highly charged with hydrogen in a state of solid solution but almost destitute of occluded hydrogen condensed on the surface. This is clearly attainable (if the hypothesis be correct) by suddenly exposing to a vacuum carbon which has been previously saturated by long contact with hydrogen at a constant temperature. Such carbon, exposed to a low pressure of hydrogen and cut off from all external influences, took up hydrogen

\* Proc. Roy. Soc., London (A), 89, 170-186, Chem. Abs. (1914), 457.  
Seventh Int. Cong. Appl. Chem., 1909.

at first (surface condensation) although already supersaturated (i.e., in respect to the solid solution), and then gave it off again in still greater quantity until final equilibrium was established. Thus the manometer first fell for a few minutes and then rose to a higher point than the initial value. In the converse case, where the interior was saturated by a very short exposure to a high pressure of gas, hydrogen was first given off, and then taken up again by diffusion into carbon. Here the manometer automatically rose for a few minutes, then steadily fell for many hours to a lower value than previously obtained. The pressure changes observed might at first seem unimportant, were it not for the one fact of great significance, viz., that (taking the second case just outlined) the higher pressure at five minutes was even less than corresponded to the gas condensed on the surface of the carbon, yet after a dozen hours had elapsed a much lower pressure was attained, a pressure which then actually did correspond to the condensed gas in equilibrium with it. Thus a considerable body of hydrogen had been transferred from the surface to the interior of the carbon. An approximate calculation of the extent of this transfer showed that the true solubility of hydrogen at the temperature of liquid air and under 2 cm. pressure was at least 4 c.c. (corr.) per gram of the cocoanut carbon employed. This absorption was roughly proportional to the square root of the pressure (whereas the total sorption varies as the cube root of the pressure). From this it appears that the dissolved hydrogen is split up into single atoms.

Tomassi\* considers that the reductions caused by hydrogen at the moment of its liberation from its compounds are wrongly attributed to its being in an allotropic condition,† such as is usually connoted by the term "nascent"; for, in that case, he argues, the same reactions ought always to follow whatever the origin of the gas; but this is not borne out by experiment.

Thus, silver chloride, bromide or iodide, suspended in water acidulated with sulfuric acid, can be reduced by the hydrogen liberated from water by electrolysis, but show no signs of reduction when the water is decomposed with sodium amalgam. Or, if a solution of potassium chlorate be acidulated with sulfuric acid, and zinc added, the chlorate is reduced to chloride; whereas if sodium amalgam be added, no reduction takes place. Nor does sodium amalgam bring about the reduction of chloric acid or of the chlorates of sodium, barium, copper, lead or mercury. In the case of potassium perchlorate, none of the usual reducing agents have any effect; zinc or magnesium with sulfuric acid, or zinc with potash or soda, or in a boiling solution of copper sulfate, all failing to bring about reduction, but, on the other hand, this is readily effected by sodium hydrosulfite — a compound from which hydrogen is not liberated. Similarly, a solution of nickel sulfate, to which potash and potassium cyanide have been added, acquires a reddish tint on the addition of zinc, while hydrogen is liberated; but if magnesium, or a magnesium-platinum couple, replace the zinc, the red color is no longer produced, although hydrogen is still liberated. Kern found (Bull. Soc. Chim., 26, 338) that by the action of magnesium on ferric chloride, ferric hydroxide was produced, and this fact Tomassi confirms, with the addition that he obtains the same result by using sodium amalgam

\* Monit. Scient., 1898 [51], 182.

† It has been suggested by Osann that active or occluded hydrogen is in an allotropic form comparable to ozone.



instead of magnesium. According to Stahlschmidt, nascent hydrogen derived from the decomposition of water by zinc dust reduces potassium nitrate to nitrite, reduced iodides and iodates, but does not reduce chlorates; and De Wilde has established the fact that sodium amalgam reduces potassium bromate, but is without action on the chlorate.

On these and similar facts Tomassi bases his opinion that the reducing power of nascent hydrogen varies according to the chemical reaction by which the hydrogen was produced, and he considers that if the gas has a greater affinity in the nascent than in the ordinary condition, this is entirely due to the hydrogen at the moment of its liberation from a compound being accompanied by the heat produced during the liberation. Hence, if nascent hydrogen be represented by the symbol  $H + a$  (in which  $a$  denotes this amount of heat), the value of  $a$  would vary with each chemical reaction, and, as a general rule, the reducing power of nascent hydrogen would be proportional to that value, provided that the reaction between the hydrogen and the substance to be reduced could once be started. There are certain cases, however, in which the reduction is due, not to the hydrogen, but to the metal which served to generate it. The reduction of potassium chlorate by means of sulfuric acid and zinc, or by electrolysis of its solution with a zinc anode, is an instance of this. If such a solution be electrolyzed with both electrodes of platinum, oxidation occurs at the anode, with the formation of perchlorate, while no trace of chloride is found at the cathode; but if a zinc anode be used, chloride is formed at the anode, but not at the cathode. From this Tomassi concluded that the reduction in this case must be attributed, not to the hydrogen, but to the zinc uniting with the oxygen of the chlorate in accordance with the equation  $\text{KClO}_3 + 3 \text{Zn} = \text{KCl} + 3 \text{ZnO}$ .

Titoff\* has studied the adsorption of hydrogen and other gases by pure gas-free cocoanut charcoal. The temperature varied from  $-79^\circ$  to  $+151.5^\circ \text{C}$ ., and the pressures from 0 to 77 cm. of mercury. The results are given in tables and the relations illustrated by isothermal and isobaric curves. Hydrogen appears to obey Henry's law for a considerable range of temperature ( $-80^\circ$  to  $+80^\circ \text{C}$ .). Titoff prefers a surface condensation theory as an explanation of the phenomena, and consequently he uses the term adsorption, rather than absorption, which would seem to suggest ordinary solution.†

Firth observes that the adsorption of hydrogen (surface condensation) by wood charcoal occupies only a few minutes, while the equilibrium due to absorption is attained only after several hours, hence "sorption" is of a two-fold character. Wood charcoal contains crystalline as well as amorphous carbon and the activity of the material depends chiefly on the latter.‡

\* Z. physik. Chem. (1910), 74, 641; see also Homfray, J. S. C. I. 1910, 1055.

† Rhead and Wheeler (Chem. Soc. Proc. (1913), 29, 51) observe that carbon, at all temperatures up to  $900^\circ \text{C}$ . and probably above that temperature, has the power of pertinaciously retaining oxygen. This oxygen cannot be removed by exhaustion alone, but may be expelled by increasing the temperature of the carbon during exhaustion. When quickly released in this manner, it appears, not as oxygen, but as carbon dioxide and carbon monoxide.

‡ Z. physik. Chem. (1914), 294; J. S. C. I. 1914, 130.

The presence of kaolin favors the combination of hydrogen and oxygen at temperatures from 230 degrees and upwards. Without the kaolin, combination does not take place until a temperature of 350 degrees or higher is reached. The activity of the kaolin depends greatly upon the temperature to which it has previously been heated, and the extent to which it has lost its water of constitution. The lower the water content, the less pronounced is the activity.\*

It has been stated by Marie † and Petersen ‡ that, in the electrolytic reduction of unsaturated acids, the nature of the cathode used has no appreciable influence upon the course and velocity of the reaction. Fokin § finds, however, that reduction can only be effected with cathodes of palladium, platinum, rhodium, ruthenium, iridium, osmium, nickel cobalt and copper, and that the quantity and the physical condition of the metal has a considerable influence on the course of the reduction. It is shown that the metals named have the capacity of occluding hydrogen, with the formation of unstable hydrides. It is these metals, also, which have been found to act as hydrogen-carriers in the reduction processes studied by Sabatier and Senderens. Fokin is of the opinion that all reduction processes taking place in presence of the metals mentioned, viz., electrolytic reduction, reduction of gaseous substances by reduced metals by the process of Sabatier and Senderens, reduction by galvanic couples, and reduction by metal hydrides in solutions, are due to a special activity of the occluded hydrogen, probably owing to such hydrogen being in the monatomic condition. The activity of the metals varies directly with their capacity of occluding hydrogen; palladium is the most efficient, and then follow, in the order given, platinum, nickel, cobalt and copper. Fokin has studied in this way the reduction of the fatty acids from linseed oil, Japanese wood oil, castor oil, cod-liver oil, and other unsaturated acids.

According to Fokin the metals can be grouped into those which, like palladium and cobalt, form definite hydrides; and those which, like platinum and nickel, have not been proved to form such definite hydrides. The latter class gives the best results in reduction catalyses. || By the action of excess of cobalt hydride at 270° C., under atmospheric pressure, oleic acid is reduced to stearic acid to the extent

\* J. S. C. I. 1914, 254, and Comp. rend. (1914), 158, 501.

† Compt. rend., 136, 1331; J. S. C. I. 1903, 1003.

‡ Z. Elektrochem., 11, 549; J. S. C. I. 1905, 895.

§ J. russ. phys. chem. Ges. (1906), 38, 419; Chem. Centr. (1906), 2, 758; J. S. C. I. 1906, 935.

|| Zeitsch. f. ang. Chem. (1909), 22, 1451-1459 and 1492-1502.

of 26 to 28 per cent, while in a sealed tube, the reduction proceeds to the extent of 60 per cent. If an ethereal solution of oleic acid be treated with palladium black, and a current of hydrogen led through, stearic acid can be detected after one-half hour; with platinum black under similar conditions, 24 per cent of stearic acid is obtained after one-half hour, 84.5 per cent after  $3\frac{1}{2}$  hours and 90 per cent after 5 hours. Oleic acid is also reduced by nickel and cobalt (prepared from the oxides), in presence of hydrogen, at temperatures of  $45^{\circ}$  to  $184^{\circ}$  C. and  $98^{\circ}$  to  $250^{\circ}$  C. respectively.\*

In order to test the view that the increased reducing power of occluded hydrogen is due to a kind of physical compression, Fokin carried out a series of experiments, which showed that compressed hydrogen (up to a pressure of 35 atmospheres) effected the reduction of unsaturated hydrocarbons more rapidly and completely and at lower temperatures than hydrogen at atmospheric pressure.†

Hydrogen reduces certain metals from their solutions, as, for instance, silver from an aqueous solution of the nitrate. The action of hydrogen on metallic solutions is much more energetic when one operates under pressure as has been observed by Beketoff.

In connection with the effect of hydrogen on metallic catalysts to alter the properties of the metal, a discussion appearing in the Metallurgical and Chemical Engineering (1913), 679, on the "Passivity of Metals," is of interest. According to Foerster and also Schmidt a metal such as iron is passive in its normal condition and only becomes active under the influence of a catalyst. Hydrogen is stated to have this catalytic effect and hydrogen ions have also the same action. Schmidt states that the most important of the catalysts which overcome the passive state of metals is hydrogen and that a small amount of it can activate large amounts of iron, nickel and chromium. The preparation of a non-pyrophoric catalyst of the nickel type by passing carbon dioxide or similar gas over it for a considerable period may perhaps depend on the elimination of the hydrogen which permits the metal to resume its normal passive state, in which condition exposure to the air does not injure the catalytic activity.

Towards hydrogen, palladium in sheet form appears to be both active and passive. In the active form the metal will rapidly absorb large amounts of the gas, while in the passive condition only slight amounts are occluded. The absorption of hydrogen proceeds in two stages; first, a rapid occlusion at the surface and second, a slow absorption into the metal mass.‡

Sieverts, Jurisch and Metz § have further investigated the solubility of hydrogen in solid alloys of palladium with gold, silver and platinum.

\*J. S. C. I., 1907, 1149.

†J. S. C. I., 1907, 169.

‡Zeitsch. phys. Chem. (1913), 513.

§Z. anorg. allgem. Chem., 322-62, 1915; Chem. Abs., 1915, 3006.

Sieverts\* has investigated the relationship between the quantity of hydrogen absorbed and the partial pressure between 138° and 821° C. and at hydrogen pressures between 1 and 760 mm., on palladium. With both commercial and pure palladium wire, between the temperature limits mentioned, the quantity of hydrogen absorbed,  $Lp$ , by unit weight of palladium is not strictly proportional to the square root of the hydrogen pressure  $p$ . The experimental results are better expressed by the equation,  $Lp = k_1 p^{1/2} + k_2 p$ , in which  $k_1$  and  $k_2$  are constants depending on the temperature; the equation is not true for higher pressures. This expression can be regarded as representing that the hydrogen molecules are in equilibrium with hydrogen atoms, both in solution in the palladium and in the gas phase, and that Henry's law holds strictly for both atoms and molecules. The dissociation constant of hydrogen is 25 at 138°; 109 at 315°; 112 at 619°, and 102 at 821° C. The quantity of hydrogen absorbed by unit weight of palladium depends only on the pressure and temperature, and is entirely independent of the surface area of the metal; consequently, the absorption of hydrogen by palladium is to be regarded as a true solution phenomenon. The isothermals of palladium-black and palladium-sponge are similar to those of compact palladium, but the actual curves differ with different specimens, and are apparently dependent on the nature of the palladium. The similarity of the absorption isothermals in all cases indicates that in palladium-black and palladium-sponge the absorption is mainly due to solution of the hydrogen, at least at temperatures above 100° C. At lower temperatures it is, however, likely that surface absorption accounts for a large portion of the hydrogen taken up. The above results are in strict accord with the statement that palladium-black and palladium-sponge are made up of varying quantities of amorphous and crystalline palladium. Both modifications appear to act as solvents for hydrogen with different powers of solution.

The method used was the same as used in previous work by Sieverts with additional precautions to ensure accuracy. The alloys were studied from 138° to 820° and with hydrogen pressures of one atmosphere and less. The velocity of the absorption and the relation between gas pressure and amount absorbed are the same as with pure metals. For all three series of alloys the amount of hydrogen absorbed per gram of alloy is approximately proportional to  $\sqrt{PH}$  and, with the exception of alloys rich in platinum, at constant pressures decreases with increasing temperature. With increasing amounts of platinum the amount of hydrogen absorbed decreases at all temperatures, probably reaching a minimum in the interval 50 to 100 per cent platinum. The higher the temperature the smaller the relative solubility lowering with constant platinum increments; at constant temperatures this lowering is smaller than proportional to the platinum content. At all temperatures, the addition of silver palladium increases the solubility of hydrogen in palladium, until a maximum is reached at 40 per cent silver, after which the solubility falls off rapidly, the effect passing through zero between 50 and 70 per cent silver. The solubility maximum obtained with 40 to 50 per cent silver increases with decreasing temperature from 800° to 270°, then decreases. Addition of gold to palladium has an effect similar to a silver addition, although not so pronounced. At 827° the solubility of hydrogen is diminished by addition of gold; at other temperatures it increases to a maximum, then diminishes. The gold concentration corresponding to the

\* Z. physik. Chem., 1914, 451-478. J. Chem. Soc., 1915, 268-269, Chem. Abs., 1915, 12; J. S. C. I., 1915, 664.

maximum solubility decreases with increasing temperature. Between 830° and 220° a given gold content results in a greater increase in solubility the lower the temperature; below 220° the relative solubility increase probably diminishes. The curves showing the variation of various physical properties with comparison in each of the binary palladium metal systems show marked similarities with the curves of hydrogen absorption in that system. The gold and silver alloys are marked by a high solvent power for hydrogen as well as by unusual electrical properties. All the evidence points to the formation of true ternary solid solutions between hydrogen and the binary alloys.

Observations (at 25° C.) have been made by Smith and Martin\* of the change of electrical resistance and cathode potential of palladium wires during their cathodic occlusion of hydrogen evolved from nitro sulphonic acid and after the interruption of electrolysis. All of the palladium wires increased in resistance by more than 56 per cent, finally reaching a value which remained unaltered by prolonged charging, but which varied irregularly from wire to wire. With small wires and ribbon (less than 0.1 mm. diameter) there was a further increase in resistance after the interruption of electrolysis, and a change of resistance whenever the charging current was changed, but these effects were not found with larger wires (0.32 mm.). The resistance of the saturated wire (less than 0.1 mm. diameter) observed during momentary interruptions of the electrolysis varied in a well-defined manner with the polarizing current, and the resistance after the interruption of the electrolysis undergoes changes which are reversible and reproducible. Considerations are given which make it probable that the changes of resistance in the smaller wires are due to processes occurring within the metal, and not far removed from its surface, and the tentative conclusion is suggested that hydrogen occluded at the cathode surface exists for some time in a transitional state in which it possesses an electrical conductivity of its own, and passes gradually into another form in which it has much less conductance, or none. A few experiments on copper wires, and a single exception on a nickel wire, show that these metals do not suffer any measurable change of electrical resistance under conditions which produce a high degree of occlusion in palladium.

Stahl† has investigated the solubility of gases in molten copper, and states that the evidence of the solubility of hydrogen is given by the surface disintegration and blister-like structure assumed by the metal during solidification after exposure to this gas. An absorption of hydrogen and diffusion through copper has been detected at 650° C. Up to 1500° C., the absorption increases almost linearly with the temperature, except at the melting-point of the metal, when a sudden increase occurs. At 650° the solubility is 0.1, and at 1500° C., 1.4 milligrams of hydrogen per 100 g. of copper. With both the molten and solid metal, the solubility increases as the square root of the pressure. The conductivity of copper is not affected by dissolved hydrogen. On heating copper containing oxide in a hydrogen atmosphere, the gas penetrates the metal and reduces the oxide with formation of water, which escapes by disintegrating the metal and rendering it unsuitable for further mechanical working. A reaction of this nature takes place in molten copper during the "polling" treatment.

Hydrocarbons are decomposed by molten copper into carbon and hydrogen, of which the former and the latter absorbed. No occlusion of any undecomposed hydrocarbon has been observed.

\* J. Am. Chem. Soc., 38, 2577-94, 1916; Chem. Abs., 1917, 8.

† J. S. C. I., 1914, 1159.

The solubility of hydrogen and nitrogen in iron has been investigated by **Jurisch** \* 100 g. of iron wire with 0.04 per cent carbon were heated in a quartz bulb and the absorption of hydrogen measured at different temperatures. Between 416° and 1450°, the solubility of hydrogen in iron increases with rising temperature, at the former temperature 0.035 milligram of hydrogen is absorbed and at the latter 1.08 milligrams. Between 850° and 900° an abnormal absorption was noticed owing to the reaction between the trace of carbon present and hydrogen to form methane, whereby the carbon content of the iron was reduced to 0.02 per cent. When slowly cooled only 0.01 milligram of hydrogen remained with the iron. Experiments with reduced iron powder previously heated for nine hours in hydrogen showed that the maximum nitrogen absorption took place at 930° when 21.65 milligrams were absorbed. At 878° only 1.58 milligrams of nitrogen were absorbed and above 930° the absorption grew gradually smaller. The above data refer to hydrogen and nitrogen at ordinary atmospheric pressure.

**Joukoff** † states that when cerium is heated in an atmosphere of hydrogen it rapidly absorbs the gas at about 350° C. Between 450° and 510° C. the dissociation pressure was about 1 millimeter so long as the proportion of hydrogen did not exceed that corresponding to cerium hydride; beyond this the dissociation pressure increased with the hydrogen concentration. It is concluded that the hydride is formed, and that this hydride is capable of dissolving hydrogen.

Theoretical considerations on hydrogenation on the basis of velocity measurements made on the hydrogenation of fumaric acid with palladium sol as catalyzer are discussed by **Korevaar** ‡ in a preliminary paper, containing no experimental results. The rate of hydrogenation of fumaric acid in the presence of palladium sol is in accordance with Nernst's surface film theory of heterogeneous reactions. The velocity was found to increase as the two-thirds power of the rate of stirring, and the temperature coefficient per 10° was 1.25, instead of 1.7, the theoretical for microheterogeneous systems. With small concentration of palladium sol, doubling the amount of sol more than doubled the rate of hydrogenation; this has been explained by **Bredig** as a common property of microheterogeneous systems due to increased Brownian movement. Since, in systems of this type, the apparent rate of the reaction is determined by the diffusion of the reacting molecules through the stationary film, at high initial concentration of fumaric acid the rate should be determined by the rate of diffusion of the hydrogen, and hence should be constant; when the concentration of fumaric acid decreases below a value determined by the hydrogen concentration and the ratio between the diffusion constants of the two molecular species, the rate should be determined by the diffusion of fumaric acid, and hence should be that of a first order reaction. This is in harmony with the experiments.

Unsaturated acids of the olefin series have been reduced electrolytically under similar conditions and their arrangement, according to ease of hydrogenation determined by **Pomilio**.§ The reductions

\* Inaug. Dissert. Leipsic, 1912; Chem. Abs., 1915, 286.

† J. Russ. Phys. Chem. Soc., 1914, 2073, Bull. Soc. Chim., 1914, 531; J. S. C. I., 1914, 1206; Chem. Abs., 1915, 566.

‡ Chem. Weekblad, 13, 98-107, 1916; Chem. Abs., 1916, 1002.

§ Z. Electrochem., 1915, 21, 444; Chem. Abs., 1916, 2576.

were carried out in both aqueous and alcoholic solutions of sulphuric acid, using a nickel gauze cathode impregnated with spongy nickel and a platinum anode. The current employed was 0.5 ampere and the temperature ranged from 25° to 90°. Electrolysis was carried on for six to twenty-four hours. In this way the rates of reduction of crotonic, allylacetic, undecylic, oleic, erucic, linoleic, linolenic, fumaric, maleic, mesaconic, citraconic, itaconic, allylmalonic and aconitic acid have been examined and the results tabulated graphically. The curves obtained show that the speed of hydrogenation depends both on the solvent and the nature of the acid. The most easily reduced acid is maleic; in the class of moderately easily reducible acids are placed citraconic and related acids, while the higher members of the series, insoluble in water, like oleic acid, are classified as difficultly reducible. Oleic acid, in fact, is reduced only very slowly either in aqueous suspension, aqueous or alcoholic soap solutions, or in turkey red oil, using a large variety of metals as cathodes 50 cc. of this acid in 0.2 H<sub>2</sub>SO<sub>4</sub> at 70° with a Ni cathode gave only 9.0 g. of stearic acid after ten hours. Erucic, ricinoleic and linolenic acids all showed little or no reduction when treated electrolytically. Of the higher unsaturated acids linolic is most easily reduced, proof, according to Pomilio that the C:C and C:O groups are in close proximity, assuming with Thiele that the reactivity depends on the relative position of these double unions.

On the assumption that, during the absorption of hydrogen, this gas and the unsaturated substance traverse a layer surrounding the particles of the catalyst and that, consequently, the medium should exert a marked influence on the rate of absorption, Böseken and Bilheimer,\* have measured the rate of reduction of pinene in various solvents with a view of obtaining data concerning this influence. In formic acid or absolute alcohol the absorption proceeded very slowly and the activity of the catalyst was seriously impaired; in anhydrous ether the rate of the absorption was diminished but the activity of the platinum was not decreased. When ethyl acetate was used as the solvent the absorption proceeded regularly at first, then decreased and practically stopped, but the activity of the platinum was not affected. With acetic acid the rate of absorption decreased without the catalyst losing its activity, and similar results were observed in the case of propionic, butyric, isobutyric, and isovaleric acids.

\* Rec. Trav. Chim. Pays-Bas., 1916, 35 288-298; J. S. C. I., 1916, 487.

## CHAPTER XII

### THE ANALYTICAL CONSTANTS OF HYDROGENATED OILS\*

The hydrogenation of oils has to such an extent changed certain of the constants by which oils and fats are at least in part identified, namely, the iodine number and the specific gravity, that the identification of a fat or fatty mixtures, often heretofore a troublesome matter at best, now promises to become even more difficult.

The reduction of the iodine number through the introduction of hydrogen into the oil, in a sense, is arbitrary; there is no difficulty in reducing the iodine number almost to zero through the hydrogenation process, or at any moment to interrupt the operation and from one and the same initial material to produce products having the most varied iodine numbers.

The specific gravity and melting point advance hand in hand as saturation progresses, the specific gravity approaching that of tristearin, while the resultant melting point in considerable measure depends upon the molecular weight and the hydroxyl content of the fatty acid components of the oil. The specific gravity of a hardened cottonseed oil whose iodine number had been reduced to zero was found by Normann and Hugel † to be 0.9999 at 15° C., while they note that tristearin has a specific gravity of 1.0101 at the same temperature.‡

The index of refraction also is strongly modified. A sample of fish oil at 56° C., according to Normann and Hugel, showed a figure of 53.8; while after hardening to an iodine number of 22.5 the index was 36° C. at the same temperature. (Scale of the Zeiss butter refractometer.)

Observations made in the author's laboratory on the index of refraction of a number of hydrogenated oils gave the results noted below:§

\* Jour. Ind. Eng. Chem. (1914), 117.

† Chem. Ztg. (1913), 815.

‡ The specific gravity of tristearin is given by the Chemiker Kalender as 1.0101 at 15° C., while Lewkowitsch reports the specific gravity of a specimen of not quite pure stearin in the melted state as 0.9235 at 65.5° C.

§ A sample of hydrogenated cottonseed oil used extensively in this country exhibited a refractive index of 1.4492 and a melting point of 59.9° C.



INDEX OF REFRACTION AT 55° C.  
 (Abbé Refractometer \*)

	Original oil	Hydrogenated oil
Corn.....	1.4615	1.4514 (M. P. 55.7° C.)
Whale (No. 1).....	1.4603	1.4550 (M. P. 41.5° C.)
Soya bean.....	1.4617	1.4538 (M. P. 50.3° C.)
Coconut oil ("olein").....	1.4429	1.4425 (M. P. 24.7° C.)
Linseed.....	1.4730	1.4610 (M. P. 42.3° C.)
Palm.....	1.4523	1.4517 (M. P. 38.7° C.)
Palm.....	1.4523	1.4494 (M. P. 44.8° C.)
Peanut (edible).....	1.4567	1.4547 (M. P. 34.7° C.)

It is of interest to note that while the addition of *hydrogen* to fatty oils reduces the index of refraction, the addition of *oxygen* increases the index as is shown in the case of blown or ozonized oils.

The gradual reduction of the index of refraction by progressive hydrogenation is shown in the following table compiled from determinations made in the author's laboratory.

Cottonseed oil was hydrogenated for a period of ten hours and samples were drawn at one-hour intervals.

	Melting point	Index of refraction, 55° C.
Original oil.....	...	1.4588
1 hour.....	28.2° C.	1.4577
2 hours.....	31.3	1.4568
3 hours.....	34.3	1.4557
4 hours.....	37.9	1.4549
5 hours.....	40.8	1.4540
6 hours.....	43.8	1.4527
7 hours.....	45.6	1.4518
8 hours.....	47.3	1.4510
10 hours.....	55.9	1.4496

The saponification number practically does not change. The content of free fatty acids changes but little. A sample of cottonseed oil containing 1.8 per cent fatty acid was found, after hardening to various degrees, to have a fatty acid content ranging from 1.4 per cent to 1.9 per cent. With sesame oil containing 2.44 per cent fatty acid the resulting hardened oil contained 2.55 per cent of acid. The content of unsaponifiable bodies does not essentially change. Cottonseed oil having 0.55 per cent unsaponifiable matter, after hardening,

\* Refraction values are given in terms of true refractive index and also according to the arbitrary scale of the butyro refractometer, in order to follow the data available, as rendered.

showed a content of unsaponifiable bodies ranging from 0.45 per cent to 0.55 per cent; sesame oil with an unsaponifiable content of 0.70 per cent, after hardening, contained 0.85 per cent unsaponifiable.

Cholesterol and phytosterol, according to **Bomer**, are not changed by treating oils with hydrogen, although this is somewhat contrary to the statement of **Windaus**,\* according to whom cholesterol may be easily reduced by the catalytic process. **Willstätter** and **Mayer**† hydrogenated cholesterol in ether solution with a platinum catalyzer.

An examination of the unsaponifiable constituents of several hardened oils has been made by **Marcusson** and **Meyerheim**‡ who used the digitonin method for the separation of sterol. The following table gives the results obtained.

UNSAPONIFIABLE CONSTITUENTS OF HARDENED OILS

	Total unsaponifiable matter		Sterol obtained by digitonin method	Sterol-free unsaponifiable components		
	Per cent	$[\alpha]_D$		Per cent	$[\alpha]_D$	Iodine number
Cottonseed oil (solidifying point 32° C.)	0.7	- 5.8	0.22	0.4	+ 6.8	....
Cottonseed oil (solidifying point 38° C.)	0.6	± 0	0.14	0.4	+ 8.1	....
Linseed oil.....	1.0	+19.5	0.21	0.7	+19	85
Castor oil.....	0.3	-10.1	0.13	0.19	+ 5.2	....
Talcol.....	0.9	- 1.9	0.10	0.7	+ 1.3	56.1
Talcol extra.....	0.9	- 3.3	0.07	0.7	....	....
Candelite.....	0.8	+ 4.7	0.05	0.7	+ 4.8	....
Candelite extra.....	0.7	+ 1.4	0.024	0.64	+ 2.8	....

The examination showed that the sterol content of hardened fats is slightly less than that of the corresponding natural fat or oil. The cottonseed oil first listed was prepared by the Wilbuschewitsch process at 150 to 160° C. with hydrogen under pressure. The second sample of the cottonseed oil was made by the Normann process, presumably at a higher temperature but without pressure. At temperatures of 150 to 160° C. apparently the difficultly reducible sterol is not affected by hydrogen and **Marcusson** and **Meyerheim** call attention to the observations of **Adamla**§ who could not hydrogenate cholesterol with a

\* Ber. d. chem. Ges. (1912), 3051.

† Willstätter and Mayer converted cholesterol quantitatively into dihydro-cholesterol by passing a slow stream of hydrogen for two days through an ethereal solution of cholesterol in the presence of platinum black (Ber., 1908 (41), 2199). (See U. S. Patent to Ellis, 1,086,357, Feb. 10, 1914.)

‡ Zeitsch. f. angew. Chem., 1914, 27, 201.

§ Dissertation. Beiträge zur Kenntnis des Cholesterins, Freiburg, 1911, 12.

nickel catalyzer at temperatures below 170° C. Marcusson and Meyerheim found cholesterol to hydrogenate readily at 195° C. while phytosterol was practically unchanged after treatment with hydrogen at 200° C. From these and other tests it was found that cholesterol is much less resistant than phytosterol to the action of hydrogen.

The content of sterol decreases with increasing melting point as shown by the following table.

Hydrogenated oil	Iodine number	Solidifying point	Sterol content
Whale oil (not hydrogenated) . . . . .	114		0 13
Talgol . . . . .	67	31	0 10
Talgol extra . . . . .	36	38	0 07
Candelite . . . . .	20	42	0 05
Candelite extra . . . . .	13	45	0 02

The unsaponifiable constituents of hardened fat when freed from sterols were of light yellow color and of salve-like consistency. These sterol-free bodies obtained from Talgol, Talgol extra, Candelite and Candelite extra, when recrystallized from benzine, yielded a product melting between 59.3° and 59.8°, which proved to be a fatty alcohol, probably octodecyl alcohol.

In the case of the acetyl number more noticeable changes take place according to Normann and Hugel. When hardening castor oil, for example, the hydroxyl number in one sample dropped from 156 to 102; in another sample the number fell to 131. The hydroxyl group is thus more or less broken down by the hydrogenation process, at least under some conditions of treatment.

#### HYDROGENATED CASTOR OIL

Acid number . . . . .	3 5
Saponification number . . . . .	183 5
Iodine number . . . . .	4.8
Acetyl number . . . . .	153 5
Acetyl number of the fatty acids . . . . .	143.1
Acid number of the fatty acids . . . . .	184 5
Saponification number of the fatty acids . . . . .	187.9
Melting point of the fat . . . . .	68° C.
Melting point of the fatty acids . . . . .	70° C.
Melting point of the acetylated acids . . . . .	47° C.

The properties of hardened castor oil have been noted by Garth\* whose observations differ somewhat from those of Normann and Hugel. As is generally known, castor oil differs materially from many

other common oils in such respects as its high viscosity, solubility in alcohol and difficulty of salting out its soaps by electrolytes. Hardened castor oil dissolves in alcohol only by heating and separates on cooling, but is soluble at ordinary temperature in chloroform. The constants of one sample of hardened castor oil examined by Garth are given in the above table.

These results obtained by Garth would indicate that the saponification and acetyl number do not change. The iodine number has fallen greatly and the melting point is much increased. The difference between the acid number of the fatty acids and their saponification number points to the formation of lactones. As is known castor oil has the property at high temperatures of forming anhydrides, accompanied by polymerization.

The effect of hydrogenation on color tests of oils is variable. Thus the Boudouin sesame oil test is not influenced; in fact the reaction seemingly is sharper after treatment of the oil with hydrogen, while the Halphen test is not likely to give positive results even with oils which have been only slightly hardened.

The Becci test is operative with slightly-hardened cottonseed oil, but is indistinct with highly-hardened oil so that this test is significant only in event of a positive coloration.

Hardened fish oil loses all its essential characteristics, such as the formation of well-defined bromine compounds of the higher unsaturated fatty acids. Thus there are obtained after hardening, new fatty acids corresponding to the saturated bodies, arachidic ( $C_{20}H_{40}O_2$ ) and behenic ( $C_{22}H_{44}O_2$ ) acids, which in variable amounts up to a proportion of 20 per cent and more have been observed in certain hydrogenated oils. In the hardening of rape oil behenic acid is formed from the erucic acid present. Other oils or fats with a noticeable proportion of acids with more than 18 carbon atoms in the molecule apparently scarcely ever come into the trade.

The complete conversion of erucic acid to behenic acid is readily obtained by reducing with hydrogen in the presence of nickel. This method has been used by Lewkowitsch in the determination of erucic acid.\*

The saturated fatty acids obtained by the hydrogenation of the unsaturated acids of Japanese sardine oil were found by Majima and Okada † to have a melting point of 75° C. and a molecular weight of 349, and consisted in the main of the higher homologues of stearic acid, such as  $C_{20}H_{40}O_2$  or  $C_{22}H_{44}O_2$ . Similar results were obtained on

\* Lewkowitsch, *Oils, Fats and Waxes*, 5th edition, Vol. I, 195 and 553.

† J. S. C. I., 1914, 362.

hydrogenating the more fluid fatty acids obtained by chilling and pressing.

As a test for hydrogenated peanut oil, **Kreiss and Roth\*** have given a method which consists in saponifying 20 grams of the oil with 40 cc. of alcoholic potash; then adding 60 cc. of alcohol and acidifying by the addition of 50 per cent acetic acid of which approximately 15 cc. are required. One and one-half grams of lead acetate are added and the mixture allowed to stand overnight. The lead salts which separate are decomposed by boiling with 5 per cent hydrochloric acid, the fatty acids are dissolved in 50 cc. of 90 per cent alcohol with slight warming and the solution is placed in water at 15 degrees for about one-half hour. The crystals which separate are recrystallized from 25 cc., then 12½ cc. of 90 per cent alcohol and the melting point determined. The presence of at least 5 per cent arachidic acid causes the melting point of the third crystallization to be over 70° C.

**Normann and Hugel†** state that this test is applicable likewise to hardened fish and rape oil. They tested a number of samples of fish oil from several sources and found in each case that the melting point of the recrystallized fatty acids was at least 70 degrees. Normann and Hugel also state that it is unnecessary with hardened fish oil to allow the lead acetate to react for several hours, it sufficing simply to let the mixture stand until cooled to room temperature; this can be hastened by cooling with water. So large a proportion of fatty acids is obtained according to this procedure that the specified amount of alcohol is not sufficient to dissolve them. It is better to use 100 to 150 cc. of alcohol and heat on the water bath until solution is effected. The application of heat should not be continued for any great length of time as arachidic acid readily forms esters. The mixture is then placed in cold water, cooled to room temperature and the separated material collected and crystallized several times from alcohol used in progressively diminishing proportions. Three crystallizations suffice for only slightly hardened fats. With fats of higher consistency one must recrystallize several times more until the melting point is constant.

In one case using hardened fish oil having a melting point of 44, three recrystallizations from alcohol gave a constant melting point of only 63 degrees, while further recrystallization using acetone caused the melting point to advance to 76 degrees. In doubtful cases one should try several solvent mediums. If the melting point is found to be above 70° C. Normann and Hugel think it proof that either hardened fish, rape or peanut oil is present. If one is certain of the unitary

\* Chem. Ztg. (1913), 58 and 369.

† Ibid. (1913), 815.

character of the oil then peanut and rape oil can be distinguished from fish oil by the cholesterol test, provided the statement of Bomer in regard to the unchangeability of cholesterol and phytosterol under ordinary conditions of oil hydrogenation is confirmed.

Data on hardened oils by Davidsohn\* are tabulated below:

	M. P.	Acid number	Saponification number	Moisture	Ash
Talgol. . . . .	39.3	3.4	191.0	0.10	0.07
Talgol extra. . . . .	46.5	3.5	191.3	0.13	0.05
Candelite . . . . .	49.0	3.2	191.0	0.20	0.08
Candelite extra. . . . .	51.9	3.9	190.8	0.15	0.04
Coryphol. . . . .	79.3	3.3	189.9	0.18	0.05

These hardened fish oils or other hardened oils put out under the trade names indicated are manufactured by the Germania Oil Works of Emmerich.

**Knapp**† states that the attention of analysts should be directed to the fact that in the immediate future they will be called upon to analyze certain new artificial fats prepared by hydrogenation and, not improbably, to detect their presence as adulterants. Thus, for example, starting with olive oil, as the absorption of hydrogen proceeds, a turbid oil, then a liquid magma, then a soft fat and finally a hard fat is obtained. Knapp observes, "A similar change occurs with all oils containing glycerides of unsaturated acids. This rise in the melting point is naturally accompanied by a decrease in the iodine value and refractive index. Fats have been prepared in this way from cottonseed oil with iodine values as low as 5, and if desired the iodine value could doubtless be reduced to 0, and the melting point raised to 60° or 70° C. While it is too costly for commercial purposes to carry the saturation of the unsaturated glycerides to completion, it might be of value in the laboratory as an aid to determining the component glycerides in a pure oil. Not only the oils containing glycerides of oleic acid can be hardened, but also those containing glycerides of linolic acid and linoleic acid (the drying oils), and even of such highly unsaturated acids as clupanodonic (in whale oils). Anyone who has seen a malodorous oil converted into a bland odorless tallow realizes the commercial possibilities of the process. And when it is remembered that the process can be stopped when the iodine value reaches a desired number, the possibility becomes evident of the preparation

\* Org. f. d. Öl- und Fetthdl. (1913), Nos. 14 and 15, and Seifen. Ztg. (1913), 529.

† The Analyst (1913), 102.

of a fat with any required analytical figures." In support of the foregoing, **Knapp** furnishes the following data:

Appearance	Original oil. Clear liquid	Hardened oils		
		Solid particles floating	Soft greasy solid	Brittle solid
Butyro-refractometer (corrected to 40° C.)	57.7	.....	.....	47.7
Fatty acids:				
Iodine value.	110	94	55	22
Titer	34.7° C.	37.0° C.	42.5° C.	52.2° C.
Neutralization value: (mg. KOH) ..	197	196	196	192

The analyst is chiefly interested in the question of how these fats are to be detected. It is doubtful if their most characteristic feature, the relatively high percentage of stearic glycerides which they contain, will be of much service. **Knapp** states that until the manufacturer accomplishes the difficult step of completely removing the nickel, the detection of traces of this metal will be the simplest and most reliable test for hardened oils.\* Although the catalyst is very finely divided, the manufacturer can obtain a perfectly clear fat by careful filtration, and hence it is the nickel contained in the nickel soaps formed by the free fatty acids present that one has to detect. The following method is suggested: 50 grams of the fat are heated in a flask with 20 cc. hydrochloric acid, with continued vigorous shaking. The mixture is allowed to separate while hot, and part of the acid solution is evaporated to dryness, dissolved in a drop of water and placed on a white tile. One drop of ammonium sulfide is added to this and also to a drop of water for comparison. **Knapp**, however, tried this test only on a few hardened oils, and in some cases with negative results. Dimethylglyoxime is a much more delicate test, but unfortunately **Pral** has found† that certain pure untreated oils give a red coloration. Hence further investigation is needed.

One of the most characteristic tests for fish oils—the bromide estimation—is quantitatively useless for these oils after hardening,

\* Too much reliance should not be placed on the nickel test as evidencing the presence or absence of hydrogenated oils. It is known to the writer that hardened oils which are free from nickel are on the market, these in some cases presumably having been prepared with the aid of palladium as a catalyzer.

† **Bomer**, *Zeitsch. Untersuch. Nahr. Genussn.*, (1912), 24, 104, and *Analyst* (1912), 87, 452.

as the percentage of ether-insoluble brominated glycerides is greatly reduced thereby. Not only are the analytical figures for the oils altered by this absorption of hydrogen, but also the traces of substances which often serve as a useful test for the particular oil in which they occur — e.g., Halphen's reaction. Knapp believes Bomer's observation that phytosterol and cholesterol are not changed in this process is of great analytical value.

Three fats obtained by Knapp from a clear cottonseed oil, hardened by hydrogen with the help of different catalysts, gave the following figures:

Catalyst	Percentage of catalyst	Character of product	Butyro-refraction (Corrected to 40° C.)	Melting point, °C.
Nickel.....	1 00	Hard	45.7	49
Platinum.....	0.10	Hard	47.8	46
Palladium.....	0 06	Brittle	45 5	52

The keeping properties of these hardened oils were found to be remarkably good. Although prepared nearly a year and a half previously and having often been exposed to damp air, yet they showed no signs of rancidity. The free acidity (0.70 per cent as oleic acid) did not appreciably change during the period of observation.

Bomer\* is in substantial agreement with the foregoing, for he states that (1) the hardened oils, as a result of the more or less complete transformation of unsaturated fatty acids (oleic, linoleic, linolenic) into stearic acid, show an increase in the melting and solidifying points as well as a lowering of the refractometer number and iodine number while the saponification number is but little altered.

(2) Judging by the iodine numbers of the liquid fatty acids, these acids appear to be not uniformly transformed into stearic acid, but the transformation of oleic acid appears to progress more slowly than the less saturated linoleic and linolenic acids, etc.†

(3) Among the hardened oils, the soft and medium-hard products, in color, consistency and in part also in odor and taste show a greater or less similarity to beef or mutton tallow, so that by external appear-

\* Chem. Rev. u. d. Fett und Harz Ind. (1912), 220.

† Muller (Seifen. Ztg. (1913), 1376) examined a hydrogenated fish or whale oil known as Talgit, having an iodine number of 49, and found the iodine number of the liquid fatty acids obtained from this material to be 100, from which he concludes that the addition of hydrogen occurs simultaneously with both the oleic and the more unsaturated acids and not successively in such a manner as to convert the acids containing two or more double bonds into oleic acid before oleic becomes transformed into stearic acid.



ance one cannot distinguish these hardened oils from such animal fats; for example medium-hard peanut oil is so completely like neutral lard, and hardened whale oil is so like mutton tallow, that one is not able to distinguish between these fats by appearance, consistency, odor or taste.

(4) Not only in their outward properties are these hardened oils like hog fat and mutton tallow, but also the usual analytical constants are so similar that one cannot distinguish some samples of hardened peanut oils and hardened sesame oil from hog fat, nor whale oil, in some cases, from mutton or beef tallow. In the latter case even the Polenske numbers agree while in the case of sesame oil they are somewhat lower than hog fat.

Oil	Appearance	Melt- ing point	Solidi- fying point	Refrac- tometer at 40°	Acid No.*	Saponi- fication No.	Iodine No.
Peanut oil un- treated . . . . .	Yellow liquid . .	.....	.....	56.8	1.1	191.1	84.4
Peanut oil hardened . . . . .	White tallowy . .	51.2	36.5	50.1	1.0	188.7	47.4
Sesame oil hardened . . . . .	White tallowy . .	62.1	45.3	38.4†	4.7	188.9	25.4
Cottonseed oil hardened . . . . .	Yellowish lard like . . . . .	38.5	25.4	53.8	0.6	195.7	69.7
Cocoanut oil un- treated . . . . .	White soft . . . .	25.6	20.4	37.4	0.3	255.6	11.8
Cocoanut oil hardened . . . . .	White lard like . .	44.5	27.7	35.9	0.4	254.1	1.0
Whale oil hardened.	Yellowish tallowy	45.4	33.7	49.1	1.1	193.0	46.8

\* Milligrams potassium hydroxide for 1 gram fat.

† Determined at 50° C.

Bomer examined a number of hydrogenated oils and tabulated the results of his investigations and from these the above condensed table has been compiled.

The solid and liquid fatty acids separated from the hydrogenated fat by the method of Farnsteiner showed the following properties:

Oil	Solid fatty acids		Liquid fatty acids	
	M. P.	Acid No.	Refraction at 40° C.	Iodine No.
Peanut oil untreated . . . . .	.....	.....	47.6	91.8
Peanut oil hardened . . . . .	.....	199.7	42.9	82.9
Sesame oil hardened . . . . .	56.4	199.5	44.7	88.9
Cottonseed oil hardened . . . . .	45.0	206.8	48.3	115.6
Whale oil hardened . . . . .	.....	199.5	44.4	96.0

Samples of these hardened oils were examined for cholesterol and phytosterol. Hardened peanut oil was found to contain 0.4 per cent, sesame oil 1.9 per cent, cottonseed oil 1.6 per cent and whale oil 0.2 per cent of sterol, of which the three first-mentioned hardened products exhibited the typical crystalline form of phytosterol. The melting point of these sterols ranged from 132° to 139° C., yielding acetates melting between about 126° and 129° C. The hardened whale oil gave a sterol melting at 149.7° C.

Bomer made a series of fractional crystallizations of hardened oil and from a sample of hydrogenated peanut oil obtained tristearin (amounting to about  $\frac{2}{3}$  per cent). Bomer has called attention to the rather striking behavior of cocoanut oil. He calculated from the iodine number that the natural oil contained 13 per cent of oleic acid and after hydrogenation approximately about 1 per cent of this acid was present. As a result of the transformation of 12 per cent of oleic acid into stearic acid, the melting point increased from 25.6° to 44.5° C., or thus 18.9° C., while the solidifying point advanced from 20.4° to 27.7° C., or only 7.3° C.

Bomer\* has studied the melting points of hydrogenated oils and as regards hydrogenated peanut and sesame oil he notes that the melting points of the least soluble glycerides are very high, being 70.6° C. and 71.5° C. respectively, while the corresponding fatty acids melted at 68.6° C. and 68.5° C.; hence these glycerides apparently consist of tristearin. The hydrogenated cottonseed oil examined yielded a mixture of glycerides of melting point 61.3° C. and derived fatty acids melting at 38° C.

A species of hardened fish or whale oil, known as "Talgit," has been examined by Müller† who found the product to have an acid value of 12.8, an iodine number of 49 and a titer (fatty acids) of 39.4° C. The fat was saponified and pressed to obtain stearic acid. It was found that the operation of pressing could be carried out effectively to yield a product technically free from liquid fatty acids; 35 per cent of solid fatty acid having a titer of 48.7° C. was thus obtained. Müller states that since mixtures of stearic and palmitic acids possess a solidifying point above 53.5° C. the low titer of the solid acids of Talgit points to the presence of solid acids other than stearic and palmitic. Dubovitz‡ thinks the low melting point to be due to the presence in the original fish or whale oil of hypogaecic and physetoleic acid or similar acids with possibly unsaturated fatty acids of a still lower number of carbon atoms.

\* Z. Untersuch. Nahr. Genussm. 1914, 153; J. S. C. I., 1914, 323.

† Seifen. Ztg. (1913), 1376.

‡ Ibid. (1913), 1445.

Leimdorfer\* regards the stearin produced by the hydrogenation of some oils to be perhaps an allotropic form of natural stearin.

The hydrogenation of linseed, peanut and sesame oil, using nickel oxide as a catalyzer, according to Bedford and Erdmann, affords approximately pure stearic glyceride.†

An attempt is made by Grimme‡ to identify fish oils after they have been hardened. As stated, the ordinary constants give no clue to the original source of a hardened oil and hence Grimme resorts to color reactions. A list of tests is given for each of the four classes of fish oils: (1) Seal oils; (2) Whale oils; (3) Liver oils; (4) Fish oils; and also characteristic tests for individual oils. These tests were also applied to two hardened oils of unknown origin and Grimme believes from his results that the color reactions are characteristic enough to establish the presence of fish oils. Nickel was found in the samples, Fortini's test (as detailed below) giving the strongest coloration. Color reactions were applied to six authentic whale oils from two different sources, and hardened to different degrees. These tests were carried out by dissolving 5 parts of the sample in 95 parts of benzene-xylene (1:1) and agitating 5 cc. of the solution with the reagent; after 5 minutes and 60 minutes the color was noted. Grimme finds the iodine-sulfuric acid reaction (1 cc. concentrated sulfuric acid and 1 drop tincture of iodine) to give a characteristic violet-red color for whale oil though the intensity of coloration decreases with increasing hardness. The constants of the six samples of hydrogenated fish and whale oils employed and the coloration produced by different reagents are tabulated by Grimme.

CONSTANTS OF HYDROGENATED FISH AND WHALE OILS

Sample	Consistency	Specific gravity	Melting point	Solidifying point	Index of refraction	Acid No.	Acid No. as free oleic acid, %	Saponification No.	Iodine No. (Wijs)
			°C.	°C.					
I.....	Lard like...	0.9256	38.5	32.8	1.4569	3.72	1.91	188.8	56.76
II.....	Tallowy...	0.9259	40.0	35.2	1.4548	8.49	4.26	189.8	49.82
III.....	Tallowy...	0.9258	42.4	36.4	1.4543	5.64	2.90	189.6	41.36
IV.....	Tallowy...	0.9263	44.8	39.3	1.4539	4.39	2.21	189.2	35.71
V.....	Tallowy...	0.9271	47.2	41.5	1.4536	4.40	2.25	188.7	26.95
VI.....	Tallowy...	0.9271	48.0	42.0	1.4530	2.18	1.10	189.3	23.18

\* Ibid. (1913), 1317.

† Jour. f. prakt. Chem., 1913, 432.

‡ Chem. Rev. u. d. Fett und Harz Ind. (1913), 129 and 155.

## COLOR REACTIONS (GRIMME)

Reagent	Color of layers	I	II	III	IV	V	VI
1 cc. conc. sulfuric acid.....	{ Acid { Fat solution	Brown Yellow	Cherry red Yellow	Cherry red Light yellow	Yellow Light yellow	Yellow Colorless	Yellow Colorless
1 cc. 70 per cent sulfuric acid.....	{ Acid { Fat solution	Light brown	Light brown	Light brown	Yellow	Yellow	Yellow
1 cc. 20 per cent sulfuric acid.....	{ Acid { Fat solution	Rose	Rose	Light rose	Light rose	Faint rose	Colorless
1 cc. acetic anhydride, then 10 drops of conc. sulfuric acid.....	{ Acid { Fat solution	Dark brown Grayish green	Brown Grayish green	Brown Grayish green	Brown Grayish yellow	Light brown Grayish yellow	Light brown Grayish yellow
1 cc. mixture equal parts conc. sulfuric acid and fuming nitric acid .....	{ Acid { Fat solution	Red brown Yellow	Red brown Yellow	Brown Yellow	Brown Yellow	Light brown Yellow	Light brown Yellow
Diluted with water after ½ hour .....	{ Acid { Fat solution	Yellow	Yellow	Bright yellow	Bright yellow	Bright yellow	Bright yellow
5 drops conc. sulfuric acid saturated in the cold with bichromate; after 5 minutes 5 cc. water..	{ Acid { Fat solution	Yellow Brownish black	Yellow Brown	Yellow Brown	Yellow Brown	Yellow Brown	Yellow Brown
10 drops fuming nitric acid.....	{ Emulsion { Acid { Fat solution	Brownish red	Brownish red	Brownish red	Brownish red	Brownish red	Brownish red
Diluted with water after ½ hour.....	{ Acid { Fat solution	Light brown then yellow	Light brown then yellow	Light brown then yellow	Yellow	Yellow	Yellow
10 drops aqua regia.....	{ Acid { Fat solution	Brownish yellow	Brownish yellow	Brownish yellow	Brownish yellow	Brownish yellow	Brownish yellow
Diluted with water after ½ hour.....	{ Acid { Fat solution	Brownish-yellow	Brownish yellow	Brownish yellow	Brownish yellow	Brownish yellow	Brownish yellow
1 cc. conc. sulfuric acid and one drop tincture of iodine .....	{ Acid { Fat solution	Violet red	Violet red	Violet red	Violet red	Violet red	Violet red

A draft of the **Codex alimentarius Austriacus**, which has been prepared by a board of prominent chemists and officials including Hefter, Wolfbauer, Fischer, Hartl and Pellischek,\* embraces the subject of hydrogenated oils and it is stated that considered as a food product these oils will require further careful investigation before it is determined with certainty just what rank they will take as edible products. It is noted that the fats now offered for edible purposes are white to yellowish in color, almost odorless and tasteless. Usually the consistency lies between that of ordinary butter and hard tallow. Now and then samples are found which melt at about 60° C. and are as brittle as carnauba wax. These hard products, of course, are not intended by themselves to be used for edible purposes, but are employed to raise the melting point of soft fats. Samples of hardened peanut and sesame oil with iodine numbers reduced to 50 or lower, sometimes down to 20, have been examined. Cocoanut oil with an iodine number of 2 or even lower has been met with. The cholesterol of animal fats and the phytosterol of vegetable oils are not altered by the hydrogenation process. The hardened fats, it is stated, scarcely ever appear on the market in their true light, but usually are put out under some trade name such as "Peanut-oleo," "Sesame-oleo," "Peanut-margarine," "Sesame-margarine," "Crisca," and the like.

Hardened oils examined by Aufrecht† in outward appearances resembled palm kernel oil. They were very hard and of granular fracture, were either pure white or yellowish in color. A distant odor was perceptible on melting or heating. The taste recalled that of tallowy fats. The products were readily soluble in the usual fat solvent mediums, but the solubility in methyl and ethyl alcohol was very slight. The fats were easily saponifiable. The content of free fatty acid fluctuated between 0.51 to 0.83 per cent. The ash reacted alkaline and consisted of alkali carbonate and traces of iron oxide, but no nickel or other constituent could be detected. The analytical results are given in table on the following page.

The detection of traces of nickel by the usual analytical methods is often difficult.‡ Dimethylglyoxime, proposed by Tchugaeff, is a reagent of great sensitiveness. Its application has been investigated by a number of chemists, and among these Bianchi and Di Nola§ report that the presence of copper and iron interferes with the test. They worked with an acid reagent and used the following procedure:

\* Seifen. Ztg. (1913), 1087.

† Pharm. Ztg. (1912), 876.

‡ Methods of determination are given by Grossmann, Die Bestimmungsmethoden des Nickels und Kobalts, Stuttgart, 1913.

§ Boll. Chim. Farm. (1910), 517.

To the substance supposed to contain nickel one or two drops of concentrated hydrochloric or nitric acid are added and the acid solution so obtained is placed in a porcelain dish, or preferably on a strip of filter paper. A few drops of ammonia are added, or in case the strip of filter paper is used, this may simply be exposed to the vapors of ammonia. The liquid is acidified with acetic acid and a drop of concentrated alcoholic solution of dimethylglyoxime is added. The presence of nickel is shown by a red coloration which grows more pronounced in the course of time. This reaction is a very simple one and does not require any particular technical knowledge for carrying out.

	1 Durotol (yellow)	2 Durotol (white)	3 Hydrogen- ated train oil
Color.....	Yellowish	White	White
Specific gravity at 15° C.....	0.9252	0.9257	0.9268
Melting point, °C.....	46.5	46.0	48.0
Solidification point, °C....	43.5	43.5	45.5
Viscosity at 50° C.....	5.4	5.4	5.6
Acid No. (calculated as oleic acid) . . .	0.51	0.57	0.83
Saponification No.....	162.2	161.0	173.5
Unsaponifiable matter (per cent)...	1.92	2.1	2.4
Acetyl No.....	1.2	1.2	0.95
Iodine No.....	3.9	4.2	7.8
Hehner No.....	95.8	95.8	96.4
Reichert-Meißl No.....	0.38	0.36	0.52
Water.....	0.0	0.0	0.0
Ash.....	0.037	0.03	0.05

Fortini\* has simplified this reaction and uses an alkaline instead of an acid reagent which apparently gives more satisfactory results than the above procedure. Fortini mixes one-half gram of dimethylglyoxime, 5 cc. 98 per cent alcohol, and 5 cc. concentrated ammonium hydroxide in the order given, yielding a clear, faintly yellowish liquid which in glass-stoppered bottles may be kept for a long time unchanged. The test is carried out as follows:

The sample to be examined is freed from fat by extraction with ether and to the residue a drop of the reagent is added. When nickel is present there will appear in a few seconds a rose-colored flock caused by reaction with the nickel oxide present on the surface of the metallic nickel. Of course, if nickel is present in the form of a soap, the fat should be extracted with, for example, aqueous hydrochloric acid in the manner prescribed by Knapp in the foregoing. In order to make the reaction even more sensitive, the residue may be heated for a few moments in an oxidizing flame to produce nickel oxide.

\* Chem. Ztg. (1912), 1461.

**Kerr**\* proposes the following modification of the dimethylglyoxime test for nickel in hydrogenated oils and fats:

Ten grams of the fat to be tested are heated on the steam bath with 10 cc. of hydrochloric acid (specific gravity 1.12), with frequent shaking for 2 to 3 hours. The fat is then removed by filtering through a wet filter paper, the filtrate being received in a white porcelain dish. The filtrate is evaporated to dryness on the steam bath, 2 to 3 cc. of concentrated nitric acid being added, after it has been partly evaporated, to insure the destruction of all organic matter. After the evaporation is complete the residue is dissolved in a few cubic centimeters of distilled water and a few drops of a one per cent solution of dimethylglyoxime in alcohol added. A few drops of dilute ammonia are then added. The presence of nickel is shown by the appearance of the red colored nickel dimethylglyoxime. The amount of nickel present may be estimated by comparing the color developed with that developed in a standard solution of a nickel salt.

The detection and determination of small quantities of nickel by  $\alpha$ -benzildioxime is described by **Atack**† as follows:

An alcoholic solution of  $\alpha$ -benzildioxime gives with nickel compounds a bulky red precipitate which is insoluble in water, alcohol, acetone, 10 per cent acetic acid and ammonia; the precipitate becomes reddish yellow on boiling. The reagent is much more sensitive than dimethylglyoxime, showing 1 part of nickel in 5 million of water, and the precipitate is readily filtered.‡ Small quantities of nickel are determined as follows: 150 cc. of a hot saturated alcoholic solution of the oxime are added for every 0.01 gram of nickel, the mixture is heated for a few minutes on the water bath, filtered, the precipitate washed with hot alcohol, and dried at 110° to 112° C.; it has the formula  $C_{28}H_{22}N_4O_4Ni$  and contains 10.93 per cent Ni. Nickel may be separated from cobalt in ammoniacal solution.  $\alpha$ -Benzildioxime is prepared by boiling 10 grams of benzil, dissolved in 50 cc. of methyl alcohol, with a concentrated aqueous solution of 8 grams of hydroxylamine hydrochloride, for 6 hours, washing the precipitate with hot water and then with a small quantity of ethyl alcohol, in which it is only slightly soluble. It may be crystallized from acetone.

According to **Lindt**, nickel may be determined colorimetrically by means of potassium thiocarbonate. Metals of the hydrogen sulfide group and manganese, cobalt and zinc should not be present.§

\* Jour. Ind. & Eng. Chem., 1914, 207.

† Chem. Ztg. (1913), 37, 773.

‡ Compare Ibbotson, J. S. C. I. (1911), 1317.

§ J. S. C. I., 1914, 335.

The hydrogen value is proposed by Fokin\* as a means of determining unsaturated organic compounds in a manner similar to the iodine values of Hubl and Wijs.

The "hydrogen value" of an organic compound is defined as the number of cubic centimeters of hydrogen (at 0 degrees and 760 mm.), which are absorbed by 1 gram of the compound. For the test an apparatus is devised consisting of a distillation flask (50 to 150 cc.) having a small beaker fused inside on the bottom, and connected by means of the side tube to a gas burette and a gasometer containing hydrogen. In the small beaker are placed about 0.1 gram of catalytic platinum, moistened with  $\frac{1}{2}$  cc. of water, and in the flask the substance to be examined and 20 to 30 cc. of alcohol free from dissolved oxygen. Hydrogen is admitted and the flask is shaken by a shaking machine until absorption is complete. The following hydrogen values were obtained by Fokin, the figures in parentheses being either the hydrogen values corresponding with Wijs' iodine value, or, where indicated, the theoretical hydrogen values. Elaidic acid, 78.6 to 81.4 (78.8); oleic acid, 86.2 to 87.2 (86.2); fatty acids from sunflower oil, 119.6 to 120.8 (122.9); fatty acids from linseed oil, 164.9 to 166.3 (166.0); castor oil, 73.7 (75.5); croton oil, 260.9 (theoretical, 258.4); undecic acid, 115.6 (114.1); erucic acid, 39.4 (65.6). Colophony does not absorb hydrogen under the conditions of the test. The "hydrogen value" of course is not a determination as yet of use in the identification of hardened oils, but is noted here because of its incidental interest.

To detect the presence of hydrogenated oil in butter fat Seidenberg † makes use of the turbidity point produced by cooling a solution of the fat in ether-alcohol. The results obtained with three samples of hydrogenated oils differed considerably, depending upon the degree of hydrogenation. The iodine numbers of these fats were determined and found to be as follows: No. 1, 73.4; No. 2, 34.5; and No. 3, 3.4. In No. 1, the amount of the saturated and less soluble glycerides is comparatively small, so that these latter do not raise the turbidity point of butter fat sufficiently to serve for their detection. The effect of the saturated glycerine produced by the hydrogenation is also seen in a comparison of the results between hydrogenated fats No. 2 and 3. In the case of No. 3, having an iodine number of 3.4, the addition of even 5 per cent can be detected with certainty, while No. 2, which has an iodine number of 34.5, can be detected in quantities of 10 per cent or above.

\* J. Russ. Phys. Chem. Soc., 40 (1908), 700; J. Chem. Soc. Abstr., 94 (1908), II, 637.

† J. Ind. Eng. Chem., 1918, 617.



The hydrogenation process has been used by **Twitchell** for the preparation of saturated fatty acids in connection with a study of the melting- and solidifying-points of mixtures of fatty acids and the use of these points to determine the composition of such mixtures.\*

Twitchell prepared three fatty acids, stearic, palmitic and behenic acid, in a fairly pure state.

The stearic acid was obtained from hydrogenated corn oil. The fatty acids from this were distilled in a current of superheated steam and the last fraction crystallized a number of times from petroleum ether and from alcohol. This stearic acid had a solidifying-point of  $69.04^{\circ}$  and a melting-point in a capillary tube of  $69.30^{\circ}$ . Its combining weight, by titration with alkali, was 284. It was not quite pure, as the last crystallization still caused a slight increase of the solidifying-point.

The palmitic acid was obtained from myrtle wax, the fatty acids of which were distilled and then crystallized several times from petroleum ether and then from alcohol. This had a solidifying-point of  $62.14$  and a melting-point of  $62.44$ . Its combining weight was 255.3.

The behenic acid was obtained from hydrogenated menhaden oil, the fatty acids of which were distilled and the last fractions crystallized ten times alternately from petroleum ether and alcohol. It had a solidifying-point of  $79.59^{\circ}$  and a melting point of  $79.99^{\circ}$ . Its combining weight was 340.9.

It can be assumed, Twitchell states, that on hydrogenating a fat, all those unsaturated acids containing 18 carbon atoms in the molecule are converted into stearic acid, all those containing 16 carbon atoms into palmitic acid and all those containing 22 carbon atoms into behenic acid. On comparing the mixtures obtained it is seen that the palmitic acid has not increased in the fatty acids of the hydrogenated product; therefore, cottonseed oil fatty acids contain no unsaturated acids with 16 carbon atoms. As the hydrogenated oil fatty acids contain 70.8 per cent stearic acid plus 2.0 per cent of oleic acid the original oil fatty acids would contain about 72.8 per cent of unsaturated acids with 18 carbon atoms, provided there was no stearic acid originally present; at any rate, it can be concluded that all the unsaturated acids of cottonseed oil have 18 carbon atoms in the molecule.

The composition of the fatty acids of cottonseed oil is therefore about as follows:

Palmitic acid.....	25.9 per cent
Unsaturated acids with 18 carbon atoms.....	72.8 per cent

The increase in weight due to addition of hydrogen, being very small, has not been considered in the above calculations.

The hydrogenated fatty acids were shown to contain 25.9 per cent of stearic, 23.2 per cent of palmitic acid and 18.7 per cent of behenic acid. The palmitic acid was present in the original oil, but the stearic and behenic acids have been formed from unsaturated acids with 18 and 22 carbon atoms, respectively.

The results indicate a composition for menhaden oil fatty acids about as follows:

\*J. Ind. Eng. Chem., 1914, 564.

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Palmitic acid.....	22.7
Other solid, saturated acids.....	11.8
Unsaturated acids with 16 carbon atoms.....	None
Unsaturated acids with 18 carbon atoms.....	26.7
Unsaturated acids with 22 carbon atoms.....	20.2
Other unsaturated acids.....	18.6
	<hr/>
	100.0

These fatty acids, therefore, probably contain about 18.6 per cent of another unsaturated acid with some other number of carbon atoms, and also 11.8 per cent of another saturated acid.

In the course of Twitchell's previous work on menhaden oil as above outlined, a fractional distillation was made of a fatty acid separated from the hydrogenated oil. There were twenty-one fractions in all. In this distillate were found behenic, stearic and palmitic acid. The presence of arachidic and myristic acid seemed probable but having neither of these acids in the pure form, Twitchell could not at that time establish their presence in any of the fractions. He therefore carried out the following investigations: \*

If any myristic acid were present it would very likely be found in the first fraction. To further concentrate it, a portion of this fraction was dissolved in alcohol, partially precipitated with lead acetate and filtered. The fatty acids were separated from the filtrate and melted in the proportion of 20 parts with 80 parts of myristic acid:

The m.p. of this mixture was.....	51.60°
That of pure of myristic acid is.....	53.76°
	<hr/>
The lowering of the m.p. was therefore.....	2.16°
The lowering of the m.p. of myristic acid by 20 per cent of palmitic acid is	4.53°
The percentage of myristic acid in the fatty acids under examination is	
therefore $100 \times (4.53 - 2.16) / 4.53 =$ .....	52.3%

which clearly establishes the presence of myristic acid in the hydrogenated oil.

**Arachidic Acid in Hydrogenated Menhaden Oil.** Fractions 15 and 16 of this same distillate had an average combining weight of 308.5 and were the most likely to contain arachidic acid. They were united and crystallized twice for 90 per cent alcohol at 15° C. The mean combining weight of the crystals was 324. In previous work it had been shown that behenic acid (molecular weight 340) was present in the hydrogenated oil. It would almost certainly be in this fraction. It remained to determine whether the reduction in combining weight was due to arachidic acid.

\* J. Ind. Eng. Chem., 1917, 582.

20 parts of the crystals melted with 80 parts of arachidic acid has a m.p. of.....	72.95
Arachidic acid has a m.p. of.....	74.78
<hr/>	
The lowering of the m.p. was therefore.....	1.83
The lowering of the m.p. of arachidic acid by 20 per cent of behenic acid.....	3.61
The percentage of arachidic acid in the crystals is therefore $100 \times$ $(3.62 - 1.83) / 3.61 =$ .....	49.3%

which establishes the presence of arachidic acid in the hydrogenated oil.

**General Results.** Having found myristic acid in both the original and the hydrogenated fatty acids in equal amounts, it was not produced by hydrogenation. On the other hand arachidic acid was found only in the hydrogenated and not in the original fatty acids. It was therefore produced by the addition of hydrogen to an unsaturated acid with 20 atoms of carbon.

The composition of the menhaden oil fatty acid described in Twitchell's paper of July, 1914,\* can now be definitely stated as follows:

	Per cent
Palmitic acid.....	22.7
Myristic acid.....	9.2
Stearic acid.....	1.8
Unsaturated acids with 16 carbon atoms.....	None
Unsaturated acids with 18 carbon atoms = 26.7 less 1.8 per cent stearic acid = .....	24.9
Unsaturated acids with 20 carbon atoms.....	22.2
Unsaturated acids with 22 carbon atoms.....	20.2

From certain observations, Twitchell concludes that the unsaturated acid with 22 carbon atoms found in menhaden oil and which, like erucic acid, is converted by hydrogenation into behenic acid, is nevertheless not erucic acid, since on fusion with caustic potash it is not converted into arachidic acid. It is probably a more unsaturated acid which is converted into stearic or palmitic acid by the fusion.

**Crossley** † reports some work carried out by Passmore on the effect of hydrogenation of a number of fatty acids and oils which is illustrated by the figures contained in the table on the following page.

A specific reaction of marine animal oils and their hydrogenation products is described by **Tortelli** and **Jaffe**.‡ The reaction depends upon the fact that these oils contain a chromogenic compound which remains unaltered even in the hydrogenation process, and towards which bromine, the reagent used, plays the part of a auxochrome, forming a coloring matter that tints with a beautiful green a chloroform solution of the oil tested.

\* J. Ind. Eng. Chem., 1914, 564.

† Pharm. Soc., Apr. 21, 1914; Pharm. J., 1914, 92, 604, 637 and 676; J.S.C.I., 1914, 1135.

‡ Ann. chim. applicata, 2, 80-98; Chem. Abs., 1914, 3723; J. S. C. I., 1914, 1061.

	% Ni Used.	Temperature.	Time in Hours	Iodine Value		Melting-point	
				Of Original Substance	Of Product	Of Original Substance.	Of Product.
Ricinoleic acid . . . . .	3	180°	2	89.8	7.99	Liquid	53°
Ricinoleic acid . . . . .	6	100°	4	91.8	3.69	Liquid	72°
Erucic acid . . . . .	10	180°	1	120.3	5.95	Liquid	58.5°
Erucic acid . . . . .	3	180°	1	74.0	2.05	34°	79°
Linoleic acid . . . . .	3	240-250°	2	182.1	30.00	Liquid	60.5°
Linoleic acid . . . . .	3	180°	2	176.0	7.79	Liquid	66°
Linoleic acid . . . . .	6	100°	3	179.2	5.98	Liquid	65°
Oleic acid . . . . .	3	240-250°	1½	82.9	4.08	Liquid	63°
Oleic acid . . . . .	1	100°	1½	82.1	9.77	Liquid	61°
Oleic acid . . . . .	6	100°	2	84.8	3.83	Liquid	63°
Whale oil . . . . .	3	180°	1½	120.0	10.30	Liquid	54°
Whale oil . . . . .	3	240-250°	1½	123.0	27.7	Liquid	48.5°
Cod oil . . . . .	3	240-250°	1½	157.0	13.1	Liquid	56°
Cod oil . . . . .	3	180°	3	159.5	11.1	Liquid	57°
Linseed oil . . . . .	3	240-250°	1½	181.2	9.52	Liquid	66°
Linseed oil . . . . .	10	180°	1½	176.8	4.75	Liquid	62.5°
Rape oil . . . . .	3	180°	1½	118.2	11.2	Liquid	59°
Rape oil . . . . .	3	100°	10½	119.1	24.3	Liquid	56°
Cottonseed oil . . . . .	3	175°	1½	101.8	18.5	Liquid	58°
Fish oil . . . . .	2	190-200°	6	124.5	51.5	Liquid	solid
Almond oil . . . . .	2	172-185	6	92.1	22.6	Liquid	

## TORTELLI AND JAFFE REACTION

The procedure is as follows: Into a graduated cylinder (with foot) provided with ground-glass stopper, and 15 mm. in diameter and 15 cc. capacity, are put 1 cc. of the oil, 6 cc. chloroform and 1 cc. glacial acetic acid. The liquid is agitated until it is homogeneous, when 40 drops of a 10 per cent chloroform solution of bromine are added the whole is again strongly agitated for a moment and the cylinder placed upon a sheet of paper. If the oil in question belongs to the group of marine animal oils it will assume within a minute a fugitive pink followed by a bright green color, becoming more and more clear and intense, and remaining so for over an hour, after which the color turns to brown or sepia. The test is sharper as the oil is more purified or refined. Vegetable oils, tested as above, remain uncolored, or at most take on a clear yellow, which does not change within an hour, then becoming orange or dull yellow. Hemp oil, however, becomes green before addition of bromine and then passes decidedly into yellow. Oils of terrestrial animals take quickly a yellowish color, which in the course of an hour always darkens to brown or sepia. Hydrogenated fats are tested as follows: A larger cylinder is used (30 mm. in diameter and about 25 cc. in capacity), into which are introduced 5 cc. of the melted fat, 10 cc. chloroform, and 1 cc. acetic acid; after agitating well, add 2.5 cc. of 10

per cent chloroform solution of bromine and agitate again. There appears almost immediately a fugitive yellowish pink, which changes in a minute to a bright green, then quickly to an intense green, lasting over an hour. Many tests were made by Tortelli and Jaffe with different oils and fats, and the color reactions were always positive. Five per cent of hydrogenated fish oil in various edible fats has been detected by this test.\*

The reliability of this color reaction is questioned by Grün and Janko.† Tests for hydrogenated fish and whale oil made according to Tortelli and Jaffe do not give good results with thoroughly hardened fats, but the color reaction is shown when incompletely hydrogenated products are used.‡ The results obtained by the author confirm this view.

The bromine reaction of Tortelli and Jaffe is stated by Davidsohn § to be of little value for the detection of marine animal oils, for many of such oils fail to give a green coloration in the test.

Hydrogenation products of marine animal oils give an intense green color, but so also do hydrogenized vegetable oils, such as linseed oil and soya-bean oil. The octobromide test of Marcusson and Huber fails with marine animal oils which have been hydrogenated or strongly heated, but is to be preferred to Tortelli and Jaffe's test, because its indications are trustworthy when a positive result is obtained.

Tsujimoto || advises that most marine animal oils give the Tortelli-Jaffe color reaction¶ especially when the oils are fresh. Old and inferior samples, however, give no coloration, or the coloration obtained is indistinct. In some cases, the coloration is given by old oils after these have been refined. The mixed fatty acids of marine animal oils as well as their distillates give the coloration, but the unsaponifiable matters and higher unsaturated fatty acids do not enter into the reaction. Hydrogenated fish oils give indistinct colorations with the test; vegetable oils and terrestrial animal oils and fats do not give a reaction.

Fryer and Weston\*\* observe that apart from the question of wilful sophistication of an oil or fat, a new problem for the oil chemist has been created by the introduction of hydrogenated oils in commerce. Chemical and physical tests may here give no indication of the natural origin of these substances and in some cases it may

\* Chem. Ztg., 1915, 14.

† Seifenfabrikant, 1915, 253-255.

‡ Seifen. Zeitung, 1915, 374.

§ Seifen. Zeit., 1915, 42, 657 and 678; Z. angew. Chem., 1915, 28, Ref., 560;

J. S. C. I., 1916, 186.

|| J. Chem. Ind. Japan, 1915, 18, 1368; J. S. C. I., 1916, 262.

¶ J. S. C. I., 1914, 1061.

\*\* Technical Handbook of Oils, Fats and Waxes, 1917, Vol. I, 64.

be impossible even to distinguish them from natural products. There are, however, certain differences in appearance and character which to the practised eye may serve to subject them to suspicion. The specific color reactions for cottonseed and apparently for sesame oil are of no avail on account of the destruction of the color-producing substances present in these oils.\* The presence of phytosterol in a stearine would prove a vegetable origin; and liver oils would still be recognized by the color reaction with sulphuric acid. A hardened maize oil might be detected by the presence of lecithin. Apart from this it would seem to be next to impossible in many cases to discover with certainty the source of an oil hardened by hydrogenation.

Pickering † considers the only likely method for the determination of the origin of hardened oils is in the separation of the liquid fatty acids, bromination of these liquid acids, and separation of the bromides. The bromides from marine animal and fish oils char on heating, while the bromides from vegetable oils and fats give a definite melting-point without any charring.

Results obtained by Sandelin ‡ on the examination of hydrogenated products prepared from whale oil at a factory in Kaipiais, Finland, and also of hydrogenated whale oil, made in Germany and offered to a Finnish margarine factory, were:

	Melting-point.	Solidifying pt.	Refractometer	Saponification	Acid value.	Iodine value	Reichert-Meissl	Polsenske value.	Mol. wt. of in-	Melting-pt of the	Nickel reaction.
		° C.	reading at 40° C.	value.		(Wijs).	value.		soluble acids.	arachidic acid	
Original whale oil.....	fluid	fluid	64.1	192.2	9.50	144.8	0.27	0.69	287.7	—	—
Artificial tallow. ....	47.5	38.1	48.9	183.7	9.88	56.9	0.25	0.49	296.4	75.5	+
Artificial stearine ...	54.3	47.3	32.4	187.7	7.80	11.7	0.14	0.31	297.0	74.1	+
Hydrogenated whale oil (German)	41.9	31.9	48.2	190.9	5.30	67.8	0.18	0.50	282.0	78.0	+

\*Of the distinguishing color reactions, the Halphen test is rendered negative by the destruction of the substance producing the color. The use of pyridine in place of amyl alcohol and a closed tube for the test has been found more sensitive and should, therefore, be employed in the case of a suspected hardened cottonseed oil to detect traces of the chromogenetic body. (Fryer and Weston, Technical Handbook of Oils, Fats and Waxes, 1917, Vol. I, 233.)

†Commercial Analysis of Oils, Fats and Commercial Products, Philadelphia, 1917, 64.

‡Teknikern, 1913, 359; Chem. Techn. Rep., 1914, 38,321; J. S. C. I., 1914, 1097.

## THE ANALYTICAL CONSTANTS OF HARDENED OILS

According to Lehmann (Chem. Ztg., 1914, 798.)

Hardened Oil.	Melting-point °C.	Solidifying-point °C.	Difference °C	Acid No. <sup>1</sup>	Saponification No	Iodine No. <sup>2</sup>	Appearance.
Peanut oil . . .	42.8	31.6	11.2	1.0	188.2	59.0	white, tallowy
Peanut oil . . . .	35.5	24.4	11.1	1.0	188.5	62.6	white, lardlike
Peanut oil. . . .	37.8	27.0	10.8	2.1	186.9	59.5	white, tallowy
Peanut oil. . . . .	37.7	26.8	10.9	. . .	. . .	. . .	white, tallowy
Sesame oil. . . . .	35.2	24.2	11.0	3.0	185.0	65.6	white, lardlike
Sesame oil. . . . .	36.9	24.4	11.5	3.1	190.2	64.9	white, tallowy
Sesame oil . . . .	35.8	24.5	11.3	. . .	. . .	. . .	white, tallowy
Cottonseed oil . .	30.0	18.2	11.8	0.3	193.7	70.9	yellow, lardlike
Cottonseed oil . .	33.6	21.8	11.8	0.4	192.5	69.0	yellow, tallowy

<sup>1</sup> Milligrams of caustic potash per gram of fat.<sup>2</sup> Huebl Method.

The iodine values of hydrogenated oils which before hardening had high iodine numbers have been determined by **Kelber and Rheinheimer** \* using the methods of Gabel, Huebl, and Wijs and concordant results were obtained by all three methods provided a sufficiently long time was allowed for the action of the iodine solution.

In determining the nickel content of hardened oil, **Lehmann** † employs the following procedure:

Two hundred grams of the fat are placed in a half liter quartz dish and are heated strongly until the fat inflames. The source of heat is removed and the fat is allowed to burn quietly. When the combustion is nearing an end, a small gas flame is placed under the dish and the considerable masses of carbon which are present are burned away, while taking care to avoid air drafts. The slight residue of ash is evaporated once with nitric and once with hydrochloric acid and is then dissolved in water and the solution concentrated. Concentrated ammonia is added to the hot solution to precipitate ferric hydrate, which is filtered off. After numerous tests with all recent methods, that of Tschugaeff for determining nickel was selected. The nickel solution is mixed with 1 cc. each of concentrated ammonia and a 1 per cent alcoholic glyoxime solution. Dilution to 50, 100 or 250 cc. is made, according to the intensity of color engendered by the red precipitate which forms. The solution is shaken vigorously and compared colorimetrically with standard solutions of known nickel content. 50 cc. portions are used for the colorimetric determination and before observation the solutions are well agitated. The results obtained by this method agreed with those obtained by the gravimetric method of Brunck.‡

The nickel content of several samples of hardened oil is shown in the following table:

\* Arch. Pharm., 1917, 417; J. S. C. I., 37, 34A; Chem. Abs., 1918, 1004.

† Chem. Ztg., 1914, 798.

‡ Zeitsch. f. angew. Chem., 1907, 1844; J. S. C. I., 1907, 643 and 1217.

## ASH OF HARDENED OIL

Oil.	MILLIGRAMS PER KILO		
	Total Ash.	Iron.	Nickel.
Peanut. ....	.....	.....	2.3
Peanut. ....	27.5	5 3	1 6
Peanut. ....	40.0	6 3	6.1
Peanut. ....	.....	.....	4 2
Peanut. ....	.....	.....	5 0
Sesame. ....	18 5	6.0	1.1
Sesame. ....	23.0	4.2	1 1
Sesame. ....	.....	.....	1.0
Cottonseed... ..	23.5	3.9	0.07
Cottonseed... ..	30.0	3.5	0.5
Cottonseed... ..	.....	.....	0.4

The ash contained in addition very small amounts of aluminum, zinc and calcium.

The detection of nickel in fats is carried out according to Schoenfeld by igniting 5 to 10 g. of the fat in a porcelain crucible. The ash is treated with 1 cc. of concentrated hydrochloric acid and heated on the water-bath, then dissolved in 2 to 3 cc. of water, filtered and the filtrate evaporated in a small porcelain dish. After moistening with a few drops of water a solution of dimethylglyoxime is added in the usual manner. Schoenfeld observed that far more certain results are obtained in this manner than by extracting the fat with hydrochloric acid, evaporating the hydrochloric acid solution and testing the residue for nickel.\*

## PRALL'S MODIFIED TEST FOR NICKEL IN HARDENED OIL

The test for nickel proposed by Prall involving extraction of the oil with hydrochloric acid, was not regarded by him as reliable under all conditions and he has found the following procedure to be more satisfactory:†

One hundred to 200 g. of the fat are burned, little by little, in a platinum dish, and the residue is ignited. The ash is dissolved in 3 to 5 cc. acidulated water, containing 5 to 10 drops hydrochloric acid. The solution is heated somewhat to remove a considerable portion of the excess of acid and is then rendered alkaline with ammonia. On allowing to stand for one hour, iron and aluminum precipitate and are removed by filtration. The filtrate is evaporated to dryness in a small porcelain dish. The residue is moistened with ammonia and then a small amount of an alcoholic solution of dimethylglyoxime is added. Even with very small amounts of nickel (0.1—0.01 m.g. in 100 g. of fat) a distinct red coloration is apparent.

\* Sicfen. Ztg., 1914, 946.

† Zeitsch. f. Unters. d. Nahrungs- u. Genussmittel, 1912, 109.



Positive results are attained only by using at least 100 g. of the fat. The most convenient method of burning off the fatty matter is to heat the sample to the fire point and allow the organic matter to quietly burn away. A blank test may be conducted by grinding nickel sulphate with oil and adding 1 cc. or 0.1 cc. (corresponding to 0.0002 g. or 0.00002 g., respectively of nickel) to 100 g. of oil, which is ignited and the residue tested as noted above.\*

#### THE EFFECT OF HYDROGEN ON OIL CONTAINING DISSOLVED NICKEL

A sample of cottonseed oil which the author hardened with about 1 per cent of reduced nickel catalyzer was allowed to stand for two years in contact with the catalyzer. The hardened fat was then melted and the catalyzer removed by filtration. The filtered fat was distinctly green in color and on analysis was found to contain 0.04 per cent of nickel. A quantity of the filtered fat was subjected to a gradual increase of temperature, while a current of hydrogen was passed through the liquid fat. Portions removed at 145° C. and again at 160° C., still had a green tinge. At 170° C., the green color practically disappeared and at 185° C. no green color could be detected although the oil was apparently unblackened by formation of precipitated nickel.

The determination of the hydrogen number is described by Albright † and although his investigations are concerned mainly with essential oils, much of the data secured is of interest in connection with the examination of fatty oils. A form of colloidal palladium was used as a catalyzer ‡ and a method of preparing material of this character is given by Albright.

The apparatus used by Albright, which is shown in Figs. 50a and 50b, is similar in principle to that devised in the organic laboratory of the University of Göttingen.

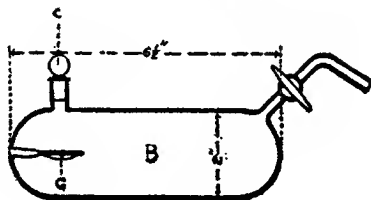


Fig. 50a.

Its fundamental parts are the camshaft, carrying four eccentrics; the shaking baskets *A*, attached to the cams and suspended from pulleys on a supporting rod; the absorption flasks *B*, which are placed in the wire baskets; the gas buret connected by means of a T tube both with the source of hydrogen and with the absorption flask. Power is supplied by a  $\frac{1}{2}$ -H.P. motor belted to the cam-shaft. When in operation, the shaft has a speed of about 200 r.p.m. Hydrogen is supplied from a Kipp generator,

\* Zeitsch. angew. Chem., Aufsatzteil, 1915, 40.

† J. Am. Chem. Soc., 1914, 2188.

‡ Paal and Amberger, Ber., 37, 124, 1904.

or from a steel cylinder and is purified by being passed through a large wash bottle containing alkaline-saturated permanganate and is washed with water at each gas buret by a separate wash bottle.

*Manipulation.* The manipulation of a reduction is as follows: The air is first displaced from the entire apparatus by passing through it a current of hydrogen, after removing the stopper *C*, and lowering the reservoir *D*, so that sufficient water remains to form an air trap at the lower bend of the buret. The levels in both arms of the U tube are then equalized at the zero mark. The three-way stopcock *E*, is then closed, the stopper *C*, which had been replaced during the flushing of the buret with hydrogen, is removed, and 0.02 g. dry colloidal palladium introduced while a current of hydrogen is passing through. Then 50 cc. of 50 per cent alcohol are added, the stopper replaced, the stopcock closed, the three-way cock *E* momentarily opened to the air to equalize the pressure in the apparatus with that of the atmosphere,

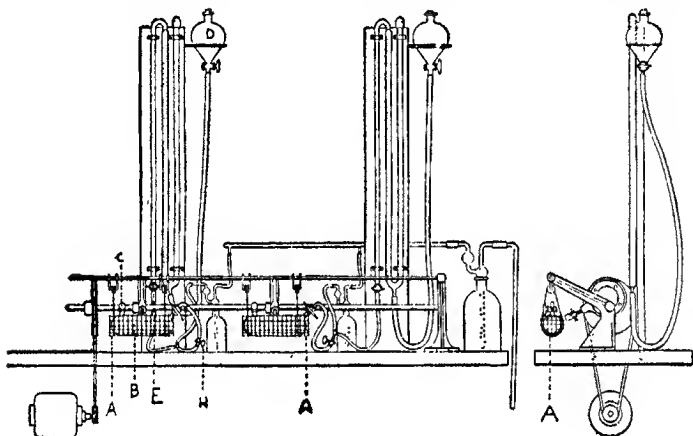


FIG. 50b.

and the flask shaken until no more hydrogen is absorbed. In this way the errors due to (1) absorption of hydrogen by the catalyzer, (2) solubility of the gas in the solvent, and (3) consumption of hydrogen by oxygen dissolved in the solvent, are removed from consideration. The buret is again filled to the zero mark with hydrogen and the shaking flask tilted until the palladium solution has drained from the concave "substance table" *G*. The substance under investigation is dropped into this table from an oil pipet (weighing bottle), again preventing the entrance of air by maintaining a current of hydrogen through the apparatus. The purpose of this "substance table" is to prevent contact between the catalyzer and substance under examination until the operator is ready to start the experiment. The stopper *C* is replaced, the cock is closed and the cock *E* opened momentarily to the air again. Connection is then made by the same stopcock between the shaking flask and the buret and the machine is at once set in motion. The absorption of hydrogen is carefully watched, maintaining the same water level in each side of the buret by regulating the flow of water from the reservoir. When the reaction is finished, a

decided and abrupt decrease in the rate of absorption occurs. On the accuracy of the observation of this point depends the accuracy of the determination. The end point may readily be found otherwise by noting the buret reading at frequent intervals, e.g., every fifteen seconds, and plotting volume against time on coördinate paper, when the break in the resulting curve will give the desired result. This point was found by drawing a straight line through the first points, then connecting with a smooth curve those points which lie at the right. The juncture of the straight line representing the main reaction, with the curved line representing absorption of hydrogen by secondary substances, if taken as the end point.

Hyland and Lloyd \* state that owing to the production of partially hydrogenated oils, having chemical and physical values practically identical with those of olive oil, which are being placed on the market as a substitute for olive oil for use in the worsted trade, etc., they have attempted to discover some test by means of which these oils could be valued. Some hydrogenated oils have been placed on the market that have an iodine value practically the same as that of olive oil, but which, unlike olive oil, gradually become tacky when exposed in thin films to moist air, such as oiled tops, etc. A study of the oxidation phenomena of various oils was, therefore, carried out but no conclusive results as regards such hydrogenated oils are reported.

A report on fats and oils by Kerr † affords a study of two methods for the detection of phytosterol in mixtures of animal and vegetable fats: (1) Bureau of Animal Industry method ‡ and (2) the digitonin method of Marcusson and Schilling.§

Three samples were sent out: (1) Lard containing 5 per cent cottonseed oil and 0.25 per cent vaseline. This amount of vaseline would effectually prevent accurate observations by the present provisional method. (2) Pure lard, rancid. Rancidity interferes decidedly with the present method. (3) Lard containing 2.5 per cent hydrogenated cottonseed oil and 2.5 per cent soya-bean oil. Three collaborators were led to correct conclusions by each method. The digitonin method is more simple and convenient but the reagent is expensive and difficult to obtain. The Bur. Animal Industry method requires more time and labor in manipulation but does not depend on an expensive reagent. Both methods are decidedly superior to the present provisional method and are recommended for adoption by the Association as provisional methods.

An investigation of the Bomer method for detecting tallow in lard by Prescher || led to the examination of fifty-eight fats of known character by both the Bomer ¶ and the Polenske \*\* methods in order to ascertain their relative efficiency in detecting foreign fats in lard.

\* J. S. C. I., 1915, 62.

† J. Assoc. Official Agr. Chemists, 1, 513-5, 1915.

‡ U. S. D. A. Bur. Animal Ind., Circ. 212.

§ Chem. Abs., 8, 1022.

|| Z. Nahr.-Genussm., 29, 433-7, 1915.

¶ Chem. Abs., 8, 1174.

\*\* Chem. Abs., 2, 716.

In the case of 25 samples of adulterated lard only 3, containing, respectively, 10, 20 and 30 per cent of beef tallow, could be detected by the Polenske method, the others, some containing as much as 15 per cent of beef tallow, giving negative tests. The Bomer method failed in only two cases, in which 5 and 10 per cent, respectively, of beef tallow were present. Eighteen samples of pure lard gave negative tests by the Bomer method, the Polenske procedure giving false indications of adulterations in two cases. Hydrogenated vegetable oils give a positive Bomer test and can be distinguished from beef tallow by the phytosteryl acetate test. The Bomer method is to be preferred for simplicity and accuracy.

A smaller amount of phytosterol acetate is obtained from oils after hydrogenation than before this treatment according to **Sprinkmeyer and Diedrichs**.\*

Hydrogenated marine animal oils are indicated according to Prescher † by the color reactions of Tortelli and Jaffe,‡ together with positive results in Kreis and Roth's test § for arachidic acid and the cholesteryl acetate test.

The presence of arachidic acid and a positive result in the phytosteryl acetate test indicate arachis or rape-seed oils. Sesame oil is detected by the Soltsien and Baudouin tests. An excessively low saponification value points to rape oil, while cocoanut and palm-kernel oils are indicated by saponification values exceeding 230 and by the Reichert-Meissl and Polenske values. Hydrogenated castor oil has a high hydroxyl value, while hydrogenated cottonseed oil may be detected by Becchi's and Hauchecorne's tests. The ratio between the iodine value and refractive index is different in hydrogenated fats from the ratio in animal fats. Cocoanut oil is distinguished by its very low iodine value. Bellier's reaction is only applicable to a limited extent to the detection of hydrogenated vegetable oils. The dimethylglyoxime test for nickel may also be inconclusive, since many freshly-expressed oils give a red coloration in the absence of nickel.

Completely hydrogenated fats have been prepared by **Mannich and Thiele** || by the aid of a charcoal-palladium catalyzer carrying 2 per cent Pd, in a container surrounded by an asbestos jacket and maintained at 100°. The catalytic material is subsequently and completely removed by filtration, yielding a product free from all contamination, an advantage stated to be not possessed by the colloidal reduction process. This method can with equal facility

\* Zeitsch. f. Unters. d. Nahrungs u. Genussm., 1914, 236; Chem. Abs., 1915, 940.

† Z. Unters. Nahr. Genussm., 1915, 30, 357; Z. angew. Chem., 1916, 29, Ref., 165; J. S. C. I., 1916, 548.

‡ J. S. C. I., 1914, 1061.

§ J. S. C. I., 1913, 201.

|| Ber. pharm. Ges., 26, 36-38, 1916; Chem. Abs., 1916, 2158; J. S. C. I., 1916, 548. See also Thiele, Dissertation, Göttingen, 1914.

be carried out in a solvent medium. The oils operated upon and the constants of the resulting fats are given below:

Oils.	M. P.	I. No.	Sapon. No.	M. P. of Insoluble Fatty Acids (Hehner).
Olive. ....	70°	0.2	190.9	71.0°
Almond. ....	72°	0.0	191.8	71.0°
Peanut. ....	64-64.5°	0.0	191.6	67.0°
Sesame. ....	68.5°	0.7	190.6	69.5°
Cacao butter. ....	63.5-64°	0.0	193.9	65.5°
Poppy. ....	70.5	0.3	191.3	71.0°
Linseed. ....	68°	0.2	189.6	70.5°
Tallow. ....	62°	0.1	197.7	64.0°
Lard. ....	64°	1.0	196.8	62.0°
Cod liver. ....	63°	1.2	186.2	59.0°

A chloroform solution of the hydrogenated cod-liver oil gave no coloration with sulphuric acid.

The effect of hydrogenation on cholesterol and phytosterol has been investigated by Marcusson and Meyerheim,\* with the following results.

Cholesterol and phytosterol were separated from the unsaponifiable matter of natural and hydrogenated oils and fats by the digitonin method of Windaus.† The amounts in natural fats ranged from 0.03 (tallow) to 0.38 per cent (linseed oil). Calculated on the unsaponifiable matter the proportion ranged from 33 to 55 per cent in the case of the vegetable oils examined, and from 8 to 14 per cent in the case of the animal fats (cod-liver oil and tallow). In addition to phytosterol or cholesterol other alcohols are present in the unsaponifiable matter, which either neutralize the optical laevorotation (as in the case of cottonseed oil) or even produce dextrorotation (linseed, cod-liver, and especially sesame oil). The presence of sesamol affords a means of detecting sesame oil, when no color reactions can be obtained. The unsaponifiable matter left after separation of cholesterol or phytosterol was a thick oil or semi-solid mass consisting in the main of unsaturated dextrorotatory alcohols (laevorotatory in the case of ox tallow) and small quantities of hydrocarbons. Only in the unsaponifiable matter of dark cod-liver oil were considerable amounts of hydrocarbons found. The dextrorotatory power of the unsaponifiable matter of sesame oil was greatly increased by the removal of the phytosterol. The iodine value (Hübl-Waller) of the residual unsaponifiable matter ranged from 56 to 78. As a rule hydrogenated fats contained less cholesterol or phytosterol than the corresponding natural fats, and the proportion decreased with the degree of hydro-

\* Mitt. k. Materialprüf., 1916, 33, 221-225; J. S. C. I., 1916, 549; Seifen. Ztg., 1916, 168. See also Willstätter and Meyer. Ber. 41, 2199; Diels and Abderhalden, Ber. 39, 884 and Moreschi, Rend. soc. chim. ital. 1914 (2) 5, 236.

† J. S. C. I., 1915, 1152.

genation. For example, the following results were obtained in the progressive hydrogenation of a marine animal oil:

	Iodine Value	Solidif Pt	Cholesterol.
		Deg. C.	Per Cent.
Original marine animal oil. . . . .	114	...	0 13
Talgol. . . . .	67	31	0 10
Talgol extra . . . . .	36	38	0 07
Candelite. . . . .	20	42	0 05
Candelite extra . . . . .	13	45	0.02

The unsaponifiable matter of hydrogenated fats after removal of the cholesterol or phytosterol was a yellow semi-solid mass, from which, in the case of talgol, and candelite, a saturated alcohol, M.P. 59.3° to 59.8° C. could be extracted with petroleum spirit. It had a refractive index of 1.4268 at 100° C. and appeared to be octodecyl alcohol. Transformation products of cholesterol were not obtained from talgol or candelite, but derivatives of phytosterol could be separated from hydrogenated vegetable oils. For example, repeated recrystallization of the unsaponifiable matter of hydrogenated linseed oil from 96 per cent alcohol yielded an alcohol (M.P. 75° C.) which did not give the characteristic phytosterol reactions.

Hydrogenated marine animal oils may be detected according to **Marcusson and Huber\*** by an examination of the unsaponifiable matter for the presence of octodecyl alcohol, M.P. 60°.

**Tsujimoto†** has prepared and examined hydrogenated chrysalis oil. He has found raw chrysalis oil to be unsuitable for the purpose of hydrogenation, as its nitrogenous and other impurities largely affect the activity of the catalyzer. The refining of chrysalis oil is by no means easy; but a method proposed by Tsujimoto, which essentially consists in heating the oil with 5 to 10 per cent by volume of dilute sulphuric acid (sp. gr. 1.39) followed by treatment with Kambara earth, gives an excellent result. The refined oil hardened by nickel catalyzer is a white fat which may be used as a raw material for soap making.

The composition of chrysalis oil has been as yet little investigated. The results of experiments previously published by Tsujimoto appear to be the only report on this subject. He has noted that the fatty acids of chrysalis oil consist of about 25 per cent saturated and 75 per cent unsaturated acids (iodine value 178.73). Among the saturated acids, palmitic acid was identified; stearic acid is probably not present. The unsaturated acids consist of oleic, linolenic and isolinolenic acids; besides them, some isomers of linolic acid are present in a larger quantity.

\* Mitt. kgl. Materialprüfungsamt, 34, 54.

† J. Ind. Eng. Chem., 1916, 802.

If the conclusions reached in the above-mentioned investigation be correct, the final product of the hydrogenation of these unsaturated acids must be stearic acid. Tsujimoto considered that a study of the product was important from the point of view of utilizing the hardened chrysalis oil for technical purposes and accordingly made certain experiments which are described below.

#### HYDROGENATION OF THE UNSATURATED (LIQUID) FATTY ACIDS OF CHRYSLIS OIL

Fifty grams of chrysalis oil were saponified in a flask with 38 cc. of 50 per cent aqueous solution of KOH and 113 cc. of 96 per cent alcohol, by warming on a water-bath; the excess of alkali was neutralized with acetic acid and 500 cc. of 7 per cent aqueous lead acetate solution was stirred into it. The resulting lead soap was twice washed with 500 cc. of hot water and treated with 500 cc. of ether at 10° C. and then filtered. (Tortelli and Ruggeri's method.) The filtrate was then treated with dilute HCl, in order to decompose the lead soap, and was well washed with water: 250 cc. of the ethereal solution of the free unsaturated acids thus obtained, which contains about 20 g. of acids of iodine value 176.17, were transferred into a strong glass bottle; 0.5 g. of Loew's platinum black was added. The bottle was then connected to a hydrogen holder. On expelling the air from the bottle by hydrogen, it was strongly shaken by means of a mechanical contrivance. After 3½ hours shaking, a loss of about 2900 cc. of hydrogen was observed on the holder. Here the hydrogenation was stopped for a time. On evaporating off the ether, a residue amounting to 17.52 g. was obtained. It was a brown-yellow crystalline mass which, when melted, formed a brown-red liquid; it melted at 56.2° C., having the neutralization value 188.92 and iodine value 45.91. The hydrogenation was apparently incomplete; but before continuing the operation, it was found better to remove the unsaponifiable and coloring matter from the product. Eleven grams of the above product were saponified with 50 cc. of 8 per cent alcoholic solution of NaOH; then 5 g. of NaHCO<sub>3</sub> and about 50 g. of pure sand were thoroughly mixed with it. The mass was dried, powdered and exhausted in a Soxhlet extractor with petroleum ether. The crude unsaponifiable matter thus extracted was 2.22 per cent. The soap in the extractor was dissolved in hot water and decomposed with dilute HCl and then taken up with ether. The ethereal solution of the fatty acids which appeared brownish yellow, was decolorized with animal charcoal, and made up to 250 cc. by adding ether; then adding 0.3 g. of the platinum black, it was hydrogenized for two hours in the same way as before (the reading of the volume of hydrogen was omitted.) On evaporating off the ether, 8.3 g. of the hydrogenated acids were obtained. The white crystalline mass had a melting-point of 68 to 68.5° C., neutralization value 195.19 and iodine value 0. This product is, therefore, a saturated compound, which in its M.P. and neutralization value nearly coincides with stearic acid (M.P. 69.3° C., neutralization value 197.5, molecular weight 284). A mixture of the product with about an equal quantity of pure stearic acid melted at 68 to 68.3° C. In order to perform the fractional crystallization of the acids, 5 g. of the hydrogenated product were dissolved in 100 cc. of 90 per cent alcohol and separated into three portions successively as follows: (1) 4.27 g.; white laminae with pearly luster; M.P. 69.5 to 70° C.; neutralization value 197.82; mean mol. wt. 283.59. A mixture with pure stearic acid melted at 69.5° to 69.7° C. (2) 0.21 g.; M.P. 68° C.;

neutralization value 197.20. (3) Residue left on evaporating the mother liquor, 0.41 g.; a little colored solid; M.P. 50° C.; neutralization value 177.42.

The low melting-point and neutralization value are probably due to the accumulation of the impurities in this part and also to the esterification of the acids on evaporating off alcohol. The result of the elementary analysis of (1) was as follows: 0.1245 gave 0.3487 CO<sub>2</sub> and 0.1439 H<sub>2</sub>O; C=76.39; H=12.84. C<sub>18</sub>H<sub>36</sub>O<sub>2</sub> required C=76.06; H=12.68. Therefore the substance is stearic acid. From the above, it was concluded that the hydrogenated product of the unsaturated fatty acids of chrysalis oil consists mainly of stearic acid.

By the hydrogenation of spinacene, a hydrocarbon from certain fish liver oils, with platinum black as catalyst, **Chapman** \* found the iodine value was reduced to 18, and a hydrocarbon, C<sub>30</sub>H<sub>62</sub>, boiling at 274° to 275° C. (18 mm.) was obtained. This was a colorless, odorless oil not solidifying at -20° C., and having a sp.gr. of 0.8172 at 20°/20° C. The unsaturated hydrocarbon squalene separated by Tsujimoto closely resembles spinacene.

The glycerol content of hardened fats was determined by **Normann** and **Hugel** † using several of the published methods and the results obtained compared with those calculated from the ester values. The results obtained by the bichromate method agreed very well with the calculated values. Wiltstätter's method ‡ gave satisfactory results, but the results obtained by the acetin method were 1½ per cent lower than the calculated values.

In the identification of hardened marine oils and rape oil, **Normann** and **Hugel** § supplement the usual melting-point test for arachidic acid by the determination of the saponification value of the fatty acids, using an excess of alkali and titrating back the excess. A direct determination with N/10 alkali is uncertain.

The behavior of the hydroxyl group of the hydroxylated fatty acids on catalytic hydrogenation by means of nickel has been studied by **Jurgens** and **Meigen** ||. Nickel catalyzer reduces castor oil below 200° practically only at the double bond of the ricinolic acid radical, while above 200° its hydroxyl group is also reduced. Ricinolic acid itself is little affected at the lower temperature but its hydroxyl group is reduced at the higher temperature. Nickel oxide catalyzer reduces the hydroxyl group more rapidly than the double

\* Chem. Soc. Trans., 1917, 56.

† Chem. Umschau, 1916, 23, 45-47. Z. angew. Chem., 1916, 29, Ref., 371; J.S.C.I., 1916, 932.

‡ J. S. C. I., 1912, 997.

§ Chem. Umschau, 23, 131-3, 1916; J. S. C. I., 1917, 658; Chem. Abs., 1917, 2736; Z. angew. Chem., 1917, 30, Ref., 108.

|| Chem. Umschau, 23, 99-102, 116-20, 1916; Z. angew. Chem., 30, II, 34, 1917; J. S. C. I., 36, 657; Chem. Abs., 1917, 2736.



bond. With 2 per cent nickel catalyzer under high pressure the hydroxyl group reduction is slower than at atmospheric pressure because the increased tension of the steam from the hydroxyl group tends to prevent further decomposition of this group.

**Svensden** \* reports on the chemical composition of hardened whale oil. A sample of hardened whale oil had acid value 1.5, saponification value 195.7, iodine number 59.8, refractometer reading at 40° C., 50; it yielded no insoluble bromide. The fatty acids consisted of 10.8 per cent of myristic acid, 17.9 per cent of palmitic acid, 10.6 per cent of Bull's C<sub>16</sub>-acid † 10.8 per cent of stearic acid, 27.7 per cent of oleic acid, 3.4 per cent of arachidic acid, 8 per cent of a solid acid, C<sub>22</sub>H<sub>36</sub>O<sub>2</sub>, 2.5 per cent of behenic acid, and 8.8 per cent of an acid, C<sub>22</sub>H<sub>40</sub>O<sub>2</sub>.

**Bosshard** and **Fischli** ‡ give the following method for the determination of hydrogen in gaseous mixtures by catalytic absorption:

The absorption of hydrogen by sodium oleate solution in presence of a reduced nickel catalyst is utilized for the quantitative determination of this gas in mixtures. The catalyst must either be used immediately after its preparation by the reduction of nickel oxide at 340° C., or it must be preserved in sealed glass tubes in 3-g. quantities in an atmosphere of hydrogen. Absorption is effected in a Hempel pipette or in a spherical pipette with a mercury seal. The gaseous mixture is freed from carbon dioxide, carbon monoxide, oxygen, etc., by the usual methods, and 15 to 20 cc. of the residue is introduced into the pipette charged with concentrated aqueous sodium oleate solution containing 3 per cent of the catalyst in suspension; the whole of the hydrogen will be absorbed after ten minutes shaking. The foam which is produced may be destroyed by allowing a small quantity of alcohol to enter the pipette, but as this retards the rate of absorption it is recommended that two pipettes be employed; when absorption is complete the gas and foam are transferred to the second pipette before adding alcohol, so that the solution in the first pipette may retain its absorbing capacity for a number of operations. Nitrogen and methane do not interfere. The latter is determined by explosion. Comparative tests show the method to be highly accurate.

**Anderson** and **Katz** § do not agree with the conclusions of **Bosshard** and **Fischli**. Commenting on the difficulties of handling the reagents, **Anderson** and **Katz** found that the reagent finally in the absorption pipette without access of air, samples of hydrogen were placed in contact with it, but with practically no absorption. Many attempts were made to obtain an active reagent, using metallic

\* *Tidskrift Kemi, Farm., og Terapi*, 1916, 20, 285-292; *Z. angew. Chem.*, 1917, 30; *J. S. C. I.*, 1917, 603.

† C<sub>16</sub>H<sub>32</sub>O<sub>2</sub>, discovered by **Bull.**, *Ber.*, 1906, 3574, but not named by him. *Chem. Abs.*, 1, 305. Named palmitoleic acid by **Lewkowitsch**, *J. S. C. I.*, 1906, 1158.

‡ *Z. angew. Chem.*, 1915, 28, 365-366; *Chem. Abs.*, 1916, 26.

§ *J. Ind. Eng. Chem.*, 1918, 24.

nickel prepared from nickel oxide of various degrees of fineness down to 200 mesh, but with no success. A temperature of 80° C. was maintained in the reagent in one case, but to no advantage. It was noticed, however, that the solutions of sodium oleate to which nickel had been added hardened much more quickly than those of the same concentration that contained no nickel. It was assumed that this was due to the "hardening" of the solution by the hydrogen absorbed by the nickel. Accordingly, the preparation of nickel was modified by substituting a current of nitrogen for the hydrogen at the point when the reduction of the nickel oxide had been completed, continuing the heating of the material for a short time to drive off occluded hydrogen. The nickel was finally cooled in nitrogen and stored in an atmosphere of this gas. When this material was employed as a catalyst, the sodium oleate showed no tendency to harden sooner than it would have done in the absence of nickel, entirely in accordance with the suggested explanation, but the reagent thus obtained did not absorb hydrogen from gas mixtures placed in contact with it.

At this juncture, the attempt to ascertain the conditions under which complete absorption of hydrogen by sodium oleate in solution might be obtained was abandoned, because of certain objections inherent in the method which would make it of little value even when standardized and found capable of giving satisfactory results. Among these objections might be mentioned the following:

1. The time and effort required for the preparation of the catalyst is considerable, and the necessity of keeping it out of contact with air adds to the difficulty of its use.
2. The reagent foams badly and this renders the absorption process itself a lengthy and tedious operation.

3. The rapidity with which even moderately dilute solutions of sodium oleate solidify renders it necessary to prepare fresh solutions frequently. Also, old solutions must be discarded before they solidify in the pipette, otherwise they can be removed only with difficulty.

The hydrogenation process is used by **Biazzo** and **Vigdorcik** \* as a means of determining colza or rape oil in olive oil. The procedure is based on the transformation of erucic into behenic acid, using palladium as catalyzer. Behenic acid is characterized by slight solubility in 90 per cent alcohol, by high melting-point (84°) and by its quantitative yield from erucic acid. Recently very cheap and powerful catalytic palladium has been prepared by **Mannich**

\* *Ann. Chim. applicata*, 6, 185-95, 1916; *J. S. C. I.*, 1917, 90; *Chem. Abs.*, 1917, 713.

and Thiele\* by depositing reduced palladium upon ignited animal charcoal, giving a catalyzer that will saturate fatty substances completely, using 1 part palladium to 15,000 parts oil.

Biazzo and Vigdoreik's method is as follows: Saponify 20 g. of the oil and extract fatty acids with ether and sulphuric acid. Dry the ether extract with calcium chloride, distill off the solvent and remove the last traces from the residue by placing in hot oven for fifteen minutes and blowing a current of air over it from time to time. Dissolve the acids obtained in 180 cc. anhydrous acetone, warm on the water-bath to incipient boiling, add 20 cc. N caustic potash and cool to 15°. Collect the precipitated fatty acids by use of the pump, wash with 4 portions of 10 cc. cold acetone, finally dissolve in water and extract from the solution the solid fatty acids with hydrochloric acid and 100 cc. ether. Wash the ethereal extract twice, each time with 100 cc. water and then shake for five minutes with 15 cc. 30 per cent aqueous solution of lead acetate, subsequently removing the subnatant aqueous layer. Filter the precipitate "A" of lead soaps from the ethereal solution "B," first allowing the liquid, if necessary, to stand on a bath at 23° to 25° for one-half hour. Examine the precipitate "A" for arachidic and lignoceric acids, i.e., for arachidic oil.† Free solution "B" from lead by use of hydrochloric acid and wash till the mineral acid is completely removed. Hydrogenate by palladium catalyzer till hydrogen is no longer absorbed, filter and evaporate the solvent. Treat the residue by fractional crystallization as in the method of separating arachidic and lignoceric acids.‡ If the final crystallization gives a substance with melting-point above 71°, the oil under examination contains a cruciferous oil. Positive indications are furnished by a melting-point between 76° to 79°. The sensitiveness of the method depends upon the care employed in preparing the palladium catalyzer, and in collecting and washing the acid potassium soaps, insoluble in acetone, at 15°.

A procedure by Kelber § relates to the removal of halogen from organic halogen derivatives by catalytic hydrogenation. Kelber notes that palladium has been used for the displacement of halogens from organic compounds, and it has been found that the reaction in presence of palladinized calcium carbonate proceeds so completely that the hydrogenation process may be used as a quantitative method for the determination of halogens.

Equally satisfactory results may be obtained with nickel catalysts and in this case it is not necessary to recover the catalyst. A special shaking tube has been designed for the use of this method for analytical purposes. This vessel is easily filled with the catalyst and the halogen derivative can be added subsequently; any contact of the liquid and catalyst with rubber connections is avoided and the product of the reaction can be quantitatively removed. The catalyst is prepared by heating basic nickel carbonate in a current of hydrogen at 310° to 320° C., cooling, and passing a current of carbon dioxide over the material. The catalyst may be kept for a long time in closed vessels. For each deter-

\* Chem. Abs., 10, 2158.

† Chem. Abs., 1917, 712.

‡ J. S. C. I., 1913, 201.

§ Ber., 1917, 305; J. S. C. I., 1917, 568 and 1916, 382 and 1130.

mination, 3 g. of the catalyst is placed in the reaction tube, shaken with water or dilute alcohol and 0.5 to 1.0 g. of alkali hydroxide in presence of hydrogen until no more of the gas is absorbed, and the substance to be analyzed is then sucked in and the funnel rinsed. Shaking is continued for some time after the reaction with the hydrogen is complete, the nickel is filtered off and washed, and the halogen in the liquid determined either gravimetrically or by titration. In the case of amino compounds or compounds which form precipitates with silver, the organic by-products should be shaken out with ether before making the halogen determination.

Commenting on an article by Moore, Richter and Van Arsdel, Lowenstein\* expresses surprise that the writers of this article made the statement that the amount of hydrogenation which is required to render the oil just incapable of responding to the Halphen test has not to their knowledge been investigated, in view of Lowenstein's Patent No. 1,187,999. In reply to this, Moore, Richter and Van Arsdale comment as follows:

In reply to Dr. Arthur Lowenstein's criticism of a section in our article on "The Incomplete Hydrogenation of Cottonseed Oil," we wish to state that U. S. Patent No. 1,187,999 was familiar to us at the time the section in question was written: neither at that time nor at the present time, however, could we regard the disclosures of the patent as constituting anticipation of our work.

The fundamental statement of the patent, as quoted above by Dr. Lowenstein, is as follows: "... the hydrogenation process is continued until a sample of the oil fails to respond to the Halphen reaction and the desired degree of crystallization takes place when the oil is chilled." There is no warrant for assuming from the language of the patent that when the Halphen test is just destroyed the proper amount of crystallizable material has just been produced; in fact it would appear that a considerable degree of choice may be exercised in the production of this stearine after the Halphen test response is gone.

The iodine number of the product of the patent is not stated to be that of a product in which the response to Halphen test has just been destroyed, but is that of a product in which both conditions have been met. The breadth of the range given, 90 to 102, indicates that "the desired degree of crystallization" upon chilling is subject to considerable variation, according to the object in view.

The other distinguishing mark given in the patent, namely, a range of increase in titre, likewise fails to disclose any definite knowledge of the degree of hydrogenation necessary to destroy the response to the test; its indication is ambiguous like that of the iodine number. We have not experimented with the Wolfbauer method, since its use is uncommon in this country, but it is certain that the range of 0.1° to 0.5° C. represents a very large range in actual hydrogenation, as measured by change in iodine number. It is noteworthy that our experiments invariably showed a decrease in titre, as measured by the A. O. A. C. method, before any increase began, so that to increase the titre 0.1 to 0.5° above that of the original oil required a drop of iodine number to about 70.

We wish to point out that if, as Dr. Lowenstein asserts, there are "many variable factors which would have an effect on this conclusion," there exists no pub-

\* J. Ind. Eng. Chem., 9, 719.

and Thiele\* by depositing reduced palladium upon ignited animal charcoal, giving a catalyzer that will saturate fatty substances completely, using 1 part palladium to 15,000 parts oil.

Biazzo and Vigdoreik's method is as follows: Saponify 20 g. of the oil and extract fatty acids with ether and sulphuric acid. Dry the ether extract with calcium chloride, distill off the solvent and remove the last traces from the residue by placing in hot oven for fifteen minutes and blowing a current of air over it from time to time. Dissolve the acids obtained in 180 cc. anhydrous acetone, warm on the water-bath to incipient boiling, add 20 cc. N caustic potash and cool to 15°. Collect the precipitated fatty acids by use of the pump, wash with 4 portions of 10 cc. cold acetone, finally dissolve in water and extract from the solution the solid fatty acids with hydrochloric acid and 100 cc. ether. Wash the ethereal extract twice, each time with 100 cc. water and then shake for five minutes with 15 cc. 30 per cent aqueous solution of lead acetate, subsequently removing the subnatant aqueous layer. Filter the precipitate "A" of lead soaps from the ethereal solution "B," first allowing the liquid, if necessary, to stand on a bath at 23° to 25° for one-half hour. Examine the precipitate "A" for arachidic and lignoceric acids, i.e., for arachidic oil.† Free solution "B" from lead by use of hydrochloric acid and wash till the mineral acid is completely removed. Hydrogenate by palladium catalyzer till hydrogen is no longer absorbed, filter and evaporate the solvent. Treat the residue by fractional crystallization as in the method of separating arachidic and lignoceric acids.‡ If the final crystallization gives a substance with melting-point above 71°, the oil under examination contains a cruciferous oil. Positive indications are furnished by a melting-point between 76° to 79°. The sensitiveness of the method depends upon the care employed in preparing the palladium catalyzer, and in collecting and washing the acid potassium soaps, insoluble in acetone, at 15°.

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Equally satisfactory results may be obtained with nickel catalysts and in this case it is not necessary to recover the catalyst. A special shaking tube has been designed for the use of this method for analytical purposes. This vessel is easily filled with the catalyst and the halogen derivative can be added subsequently; any contact of the liquid and catalyst with rubber connections is avoided and the product of the reaction can be quantitatively removed. The catalyst is prepared by heating basic nickel carbonate in a current of hydrogen at 310° to 320° C., cooling, and passing a current of carbon dioxide over the material. The catalyst may be kept for a long time in closed vessels. For each deter-

\* Chem. Abs., 10, 2158.

† Chem. Abs., 1917, 712.

‡ J. S. C. I., 1913, 201.

§ Ber., 1917, 305; J. S. C. I., 1917, 568 and 1916, 382 and 1130.

## CHAPTER XIII

### EDIBLE HYDROGENATED OILS

Since the addition of less than 1 per cent of hydrogen suffices to convert cottonseed oil or other vegetable oils into a fatty body of at least the consistency of lard, it follows that manufacturers of ordinary lard compound (that is to say, a mixture of about 85 to 90 per cent of refined cottonseed oil and 10 to 15 per cent or so of oleo-stearin) have promptly turned their attention to the production of compound by a "self-thickened" cottonseed oil.

The high cost\* of oleo-stearin prevailing during recent years makes the method an attractive one and the hydrogenated product from cottonseed oil has the advantage, if properly made, of being very stable in character. Unquestionably, also, the hardening process is destined to increase the demand for cottonseed oil in the manufacture of edible fats.

By the hydrogenation process a lard substitute may be prepared in two ways. The entire oil may be simply hardened to the consistency of lard, care being taken to employ an oil as nearly neutral as possible to prevent excessive solution of catalytic metal, and to avoid a high temperature of treatment so as not to impair the flavor of the product. If the color and flavor are detrimentally affected, resort may be had to a further treatment with fuller's earth followed by steam-vacuum deodorization. The addition of a small amount of coconut oil benefits the flavor.

The other method is that of making lard compound which, as indicated above, involves thickening a large proportion of normal oil with a small amount of a relatively-hard hydrogenated product. This may be carried out as follows:

After the oil has been hardened, it is freed of catalyzer and then may be run into tanks containing the requisite amount of deodorized cotton oil (or other edible oil) and if necessary the mixture is further clarified and filter-pressed. With hardened cotton oil of 58 to 60

\* Even though there may exist no marked price differential between oleo-stearin and hardened cottonseed oil, yet when, as is the case, millions of pounds of lard compound are made monthly in this country, a reduction in cost of but a small fraction of a cent per pound means an important gross saving.

titer, only 7 to 10 per cent is required to thicken the oil to the consistency of lard, although in hot climates a somewhat larger proportion may be needed.\* The mixture is run onto a chill roll to cause rapid solidification and after slight aeration to improve the color

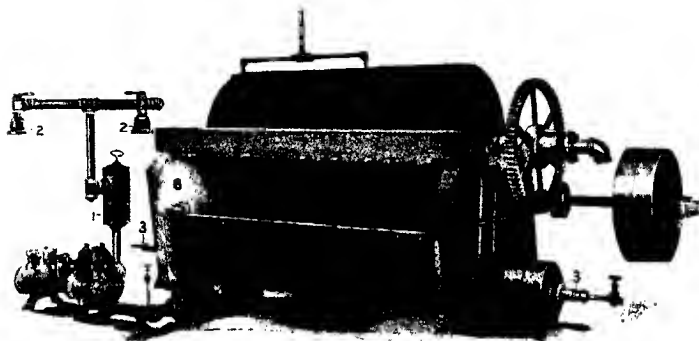


FIG. 51.

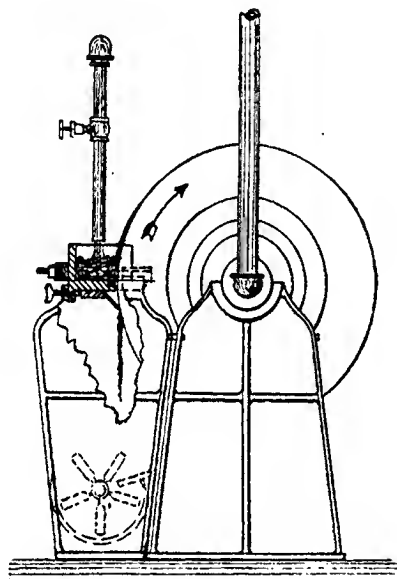
is ready to be packaged. Fig. 51 shows a chill roll or lard cooler of the type usually employed.

In this illustration the large upper cylinder or roll is chilled by the circulation of brine and is slowly rotated say from 6 to 10 r.p.m. The hot liquid compound at a temperature of 50° to 55° C. is run into the feeding trough 7 and falls onto the chilling roll, forming a thin somewhat translucent film which quickly cools and solidifies. The solid fat is removed by a scraper and falls into a picker trough 5. The latter contains a shaft equipped with beating and conveying blades which churn the composition and destroy the translucency, producing an opaque white product of lard-like appearance. The picker is run at a relatively high speed, say 175 to 180 r.p.m. Fig. 52 is an end view showing chill roll, feeding trough and picker. Fig. 53 is an illustration of a modified type of compound cooler. In Fig. 54 the cooler and picker appear on the left hand and in the center is a pump which withdraws the product from the picker and forces it through the pipe line to the packaging cocks on the right hand. Too high a

\*An object in making lard compound is to use as large a percentage of cottonseed oil as possible and yet fulfil the required conditions as to the stiffness of the material to withstand warm temperatures without much softening. Compound which stands a moderately warm climate can be made with even as low as 6 to 7 per cent hardened oil.

speed of the picker blades incorporates an excessive amount of air in the product rendering it "fluffy."\*

The speed of rotation of the chilling roll is governed by the rate of feed and temperature of the brine. The latter may be kept between, for example,  $-5$  to  $+10^{\circ}$  F. for good results. If the brine is too cold, the product is liable to drop badly from the roll and the texture



END VIEW.

FIG. 52.

is not always satisfactory. This, however, may be largely remedied by increasing the feed. In winter the brine may be held at a slightly higher temperature to prevent brittleness. In the hottest weather, very cold brine should be used to aid in securing a product which will preserve its color and consistency for a considerable time.

When properly made the compound derived by the hydrogenated oil thickener is excellent in color, texture, flavor and keeping qualities. By many it is considered superior in several respects to oleo-stearin compound.

\* The author desires to make acknowledgment to the Allbright-Nell Co. of Chicago and the Brecht Co. of St. Louis for their courtesy in furnishing the illustrations Figs. 51 to 54.



Possibly, however, for best results as to stability it is desirable to hydrogenate the entire body of oil to a fatty acid titer of 36 or 38, or whatever consistency may be required, rather than to take a relatively small proportion of the oil and harden it to a titer of 50 to 60

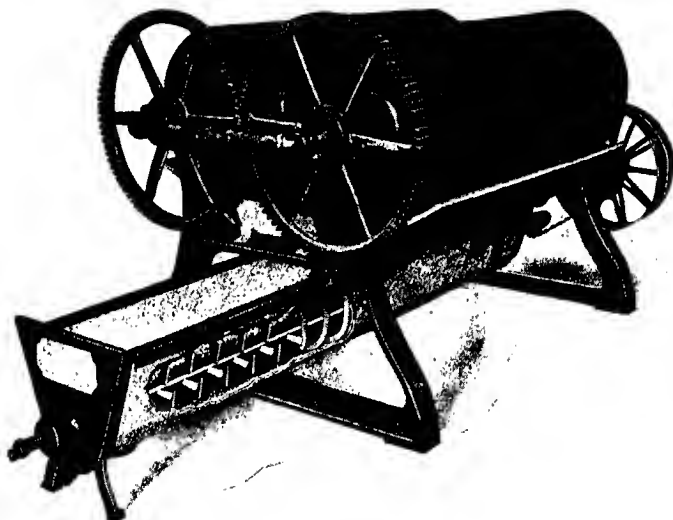


FIG. 53.

or thereabouts and incorporate with unhydrogenated oil. It appears that the hydrogenation of the total body of the oil, by transforming the linoleic and linolenic compounds and the like, has a tendency to improve the oil as regards its edibility and certainly gives it greater stability. The flavor of lard compound is, however, preferred by

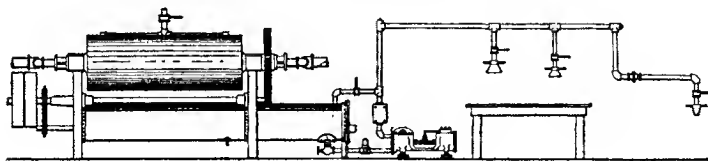


FIG. 54.

many large users of lard substitute presumably because of the proportion of normal oil which it contains, and the manufacturing cost is lower.

Finally, it may be stated, by partial saturation of glycerides, we have the possibility of preparing from tri-olein the oleo-distearin

or the dioleostearin. Dioleopalmitin would give either oleosteapalmitin or distearopalmitin. From tri-olein we may have the two isomeric oleo-distearins,  $\alpha$ - and  $\beta$ -oleo-distearin as well as  $\alpha$ - and  $\beta$ -dioleostearin. Which of these we may be able to produce controllably and which may prove best from the edible standpoint are problems for the future to solve.

Joslin\* calls attention to the economy in using hardened oil "vegetable stearin" in place of oleo-stearin for making lard compound, since only 7 to 10 per cent of the former is called for against 14 to 20 per cent of the oleo-stearin. Of course the amount of hardened oil required depends on its degree of "hardness" but for the present grades of hydrogenated cottonseed oil of 58 to 60 titer, now on the market, the above proportions hold. When the oil is hardened to about the consistency of average oleo-stearin, naturally a greater proportion is needed in lard compound.

Joslin notes the resultant economy by the employment of hardened oil at one plant during a period of one year.

93 parts cottonseed oil at 6.45 . . . . .	\$6.00
7 parts hardened oil (vegetable stearin) at 9.25 . . . . .	.65
Cost per hundred pounds of compound . . . . .	<u>\$6.65</u>
86 parts cottonseed oil at 6.45 . . . . .	\$5.55
14 parts oleo-stearin at 9.25 . . . . .	1.29
Cost per hundred pounds of compound . . . . .	<u>\$6.84</u>

Or a saving of practically 20 cents per hundred pounds of compound manufactured.

Hydrolceithin has been prepared from lecithin by Riedel.† A hardened fat called "Brebesol" intended for edible purposes is manufactured by the Breinen Besigheimer Ölfabriken.‡

#### EDIBILITY OF HYDROGENATED OILS

It seems to be generally accepted by those who have investigated the matter carefully that the hydrogenated oils have as desirable a degree of edibility as the oils from which they are derived. It is even claimed that by destroying traces of certain unsaturated bodies thought to be slightly toxic in nature, hydrogenation renders the oil better adapted for human consumption.

\* National Provisioner 1914, 17.

† Method of Preparing Hydrolceithin. German Patent. Compare Paal and Oehme, Ber., 1913, 1297.

‡ Seifen. Ztg., 1914, 263.

A question of serious import has, however, arisen in the use of nickel catalyzer. Aside from the fact that by careless filtration traces of the suspended nickel may be present in the product, there is the more serious problem of the actual solution of nickel to form nickel soaps which cannot be easily removed.

According to **Bomer**,\* nickel is dissolved by oils during the hydrogenation treatment only when the oil contains free fatty acid in considerable amounts. A sample of hydrogenated sesame oil containing  $2\frac{1}{2}$  per cent of fatty acid was found to contain 0.01 per cent ash with 0.006 per cent nickel oxide. Whale oil, containing 0.6 per cent fatty acid, yielded 0.006 per cent ash and 0.0045 per cent nickel oxide. Such an amount of nickel possibly would be regarded as undesirable or objectionable in a product intended for edible purposes.†

\* *Zeitsch. Nahr. Genussm.* (1912), 104 and *Chem. Rev. u. d. Fett. u. Harz. Ind.* (1912), 221.

† In a discussion of Bomer's paper (loc. cit.) Lehmann asked whether nickel was found in sufficient amounts to make a quantitative determination in hydrogenated oils, and Bomer replied that the amount of nickel was just so much larger the greater the amount of free acid in the oil and the longer the action of the catalyzer on the oil; while Prall observed that the nickel content of hardened oil depended essentially upon the amount of free acid and that one should reduce the free fatty acid to the lowest possible amount, that with 0.2 per cent free fatty acid in the oil no nickel had been detected in the hardened products examined. One could say, however, that in 100 grams of oil a fraction of a milligram of nickel is detected. Lehmann then remarked that presumably it was to be understood that the presence of nickel could not be avoided and that one-half a milligram of nickel in 100 grams of the oil would be a good result, to which Prall replied that this was the case when the acid of the oil was well removed.

Auerbach (*Chem. Ztg.*, 37, 297) regards the 0.000002 per cent or so of nickel which remains in hydrogenated oil to be of no practical moment from the standpoint of edibility.

An oil mill in Europe making high-grade peanut oil is now constructing a plant for hardening edible oils by a hydrogenation process that is said to afford a product free from the objectionable traces of nickel found in most of these oils. The hardened oil will be sold to the margarine factories.

Lehmann stated (Bomer, loc. cit.) that we need have no great concern over the utility of this fat or of its physiological action; Straub noted that samples of the hardened oil melted at 53° C. and that fats of such high melting point or in fact any fat melting above 37° C. were not suitable for persons affected with certain maladies of the digestive tract. Lehmann remarked that the work carried on in the Voit laboratory indicated high melting point fats to be injurious, but considering the way hardened fats are made, apparently the means were at hand to make the melting point high or low at will; that fats which were to be eaten must not, of course, have a melting point of 53° C. Bomer added that he was of the opinion that hardened fats were not as beneficial as oil, but that was not the question. The widespread use of edible oils depended on the fact that edible fats must have a certain measure of consistency. Margarine melting at 20 degrees required but a slight addition of

The use of nickel in the form of an oxide, or the use of nickel catalyzer containing a considerable proportion of oxide, is perhaps undesirable from the point of view of solubility in oil. Nickel, in the metallic state, cannot combine with a fatty acid to produce a soap, except with the elimination of hydrogen, and in the presence of an atmosphere wholly of hydrogen, because of mass action, such reaction would not be likely to take place. On the other hand, nickel in the form of oxide would yield water on combining with fatty acid which would be yielded practically into a vacuum as regards the vapor pressure of water. Hence in the manufacture of products intended for edible purposes it is suggested that conditions be maintained such that the catalyzer, if of the nickel type, is preserved almost wholly in the metallic state. Also it is desirable to not force the reaction too rapidly with the consequent danger of breaking down the carboxyl group and setting free water which would react to produce fatty acid.\*

a fat melting at 50 degrees. It was not, therefore, a question of the melting point of the hardened oil, but of the melting point of the margarine or other edible fat and the hardened oil was employed simply to adjust the melting point, the same way as beef tallow and the like were used.

A synopsis of Bomer's paper (*Z. Nahr. Genussm.*, 24, 104-113) appearing in *Chemical Abstracts*, Nov. 10, 1912, 3201, concisely expresses his work. Samples of peanut, sesame, cottonseed and whale oil were hardened. The analyses of the resulting products indicate that the more completely unsaturated fatty acids (oleic, linolenic and linoleic) are converted into stearic with increase in the melting point and the lowering of the iodine number, while the saponification number is scarcely altered. The iodine number of the liquid acids seems to indicate that the less saturated acids are more rapidly converted into stearic than is oleic. The partially saturated products resemble lard in color, taste and odor, while those obtained by further hardening are very similar to beef or mutton tallow. The ordinary constants of the hardened peanut oil are so similar to those for lard that it is very difficult to distinguish it from hog fat, but the phytosterol of the 3 vegetable oils investigated was not affected by the treatment, so that the phytosterol acetate test may be relied upon for the detection of these artificially hardened fats when they are used as adulterants for lard, margarine, etc. Cottonseed oil, after treatment, no longer gives the Halphen reaction, but sesame oil still responds to the Baudouin test. Where nickel is the catalytic agent traces of it will be found in the finished product if there were any appreciable amount of free acid in the original oil. Bomer concludes with a brief report of preliminary work on the stereo-chemistry of the glycerides formed and the requirements which the new product will have to meet to be acceptable as a human food.

\* Bouant (*La Galvanoplastie* (1894), 186) makes the comment that after having considered nickel as dangerous in the preparation of food, it is now recognized, on the contrary, to be harmless. Langbein (*Electro Deposition of Metals* (1909), 246) observes that hot fats strongly attack nickel. (*Trans. Am. Electrochem. Soc.*, 23, 116 (1913).)

In the course of some investigations by Gates (*J. of Phys. Chem.* (1911), 15,

The investigations of various authorities, such as Lehmann, Thoms and Müller have shown that hardened oils used for edible purposes do not cause any derangement of the system and that they are the complete equivalent of animal and vegetable fats of like melting point.\* Hydrogenated fats are used just like ordinary fats and do not hinder the assimilation of other food constituents. The nickel content on a daily consumption of 100 grams of the hardened fat is stated to amount at the most to 0.6 mg. and may be regarded as entirely uninjurious. Hardened fat possesses extremely good keeping qualities, and this is probably also the case with margarine prepared from it.† Leimdorfer observes that hydrogenated fats change in odor and color when preserved even in a vacuum.‡

A careful study of the occurrence of nickel in edible products of various kinds has been made by Normann and Hugel.§ Hardened fats prepared with the aid of nickel catalyzers, and intended for edible purposes, contain traces of nickel which they state amounts to two parts per million. But fats which have been treated in nickel-lined receptacles show fully this content of nickel. Nickel-lined ware has

97) it was observed that many of the common metals are dissolved appreciably by oleic, palmitic and stearic acids, with evolution of hydrogen.

The Bureau of Animal Industry of the Department of Agriculture is investigating the matter and apparently intends to determine the relative degree of toxicity of the traces of nickel in the form existing in improperly made hydrogenated oil. We may add that, so far as can be ascertained, the Department looks kindly upon the advent of hydrogenated oil in view of the likelihood that it is destined to prove a very acceptable substitute for higher-priced animal fats and does not propose, according to our understanding, to venture any ruling until the matter has had protracted scrutiny.

The editor of the National Provisioner comments on the foregoing as follows:

"It is evident that the government investigations have resulted favorably, since stearine made by this process is recognized and passed by the Bureau in meat inspection, the only requirement being that it shall be stated on the label that it is 'Stearine made from cottonseed oil' to indicate that it is manufactured stearine rather than the natural article." Editorial note in National Provisioner, Dec. 27, 1913.

Thompson notes that some criticism has been directed at the use of hardened oils for edible purposes on the ground that nickel is used in the process, but the manufacturers say that although nickel is generally used none of it is left in the oil, and that even if it were it is harmless, as shown by many tests with animals and with human "poison squads." Consular & Trade Reports, Dept. of Commerce, Jan. 14, 1914, 171.

\* See also "Gehartete Pflanzenfette in der Speisefettindustrie," Der Seifenfabrikant, 1914, 181.

† Halbmonatschr. f. d. Margarine-Ind., 1914, No. 4, 37; Seifen. Ztg., 1914, 206.

‡ Seifen. Ztg., 1913, 1317; J.S.C.L., 1914, 206.

§ Seifen. Ztg., 1913, 959.

been in use for ten years or more and during this period many people have eaten foodstuffs containing nickel, without any injurious effects being noted. Two publications have already discussed the matter to some extent, one being by Ludwig\* and the other by Lehmann.† In one kilo of various foodstuffs these investigators found the following content of nickel:

Ludwig		Lehmann	
Spinach.....	25-27 mgs.	Beef and bouillon. ....	26-64 mgs.
Peas . . . . .	12-16 "	Potato pulp (equal part	
Lentils (acid) . . . .	35 "	of water).....	26-40
Lentils (boiled) . . . .	24 "	Spinach . . . . .	22.4
Sourkraut . . . . .	54-129 "	Damson plum mixture...	13.3
Plums . . . . .	35 "	Sourkraut. . . . .	18-57
		Fruit cooked in 2 per cent	
		acetic acid solution . . .	65-67
		Water, salt water, flesh	
		extract and milk. ....	3.5-5.3

The whole question appeared of sufficient importance to lead Normann and Hugel to repeat this work. They used a nickel kettle to prepare the food material and ignited the product in a silica vessel to obtain the content of ash. Hydrochloric acid was then added to the ash and the nickel determined by Tschugæeff's reagent.‡ In this manner the nickel was determined gravimetrically in all cases, with the exception of coffee. In this latter case a colorimetric comparison with a nickel solution of known content was made.

Thus Normann and Hugel found:

	Duration of cooking, hours	Mgs. of nickel in one kilo of material
Coffee.....	$\frac{1}{2}$	0.03
Apple.....	$\frac{1}{2}$	46
Cabbage.....	$\frac{1}{2}$	83
Red cabbage.....	1	67
Sourkraut.....	$1\frac{1}{2}$	127
Kohlrabi.....	1	19
Potato.....	$\frac{1}{2}$	80

One of these investigators used a kettle of this character for a considerable period in his household. The food for the use of the family was cooked in the kettle so that food with a nickel content, approximating that of the above tabulation, was eaten, but no ill effects were observed.

\* Osterr. Chem. Ztg., Vienna, Vol. I, No. 1, 1898.

† Arch. für Hygiene, Vol. 68 (1909), 421.

‡ Zeitsch. f. angew. Chem., 1907, 1844.

The determination of nickel in fats was made by igniting 200 grams of the fat in a silica vessel, dissolving the ash in hydrochloric acid, saturating the solution with ammonia, filtering to remove any precipitate of iron or alumina and evaporating the filtrate. To the residue was added 1 cc. of Tschugaeff's reagent (alcoholic solution of dimethylglyoxime) and ammonia (when a rose coloration due to nickel occurs). To determine the nickel quantitatively, the whole residue was dissolved in 100 cc. of water and the coloration compared with the color produced by adding the reagent to solutions of nickel chloride of known content. To secure a constant shade it was found desirable to allow the solution as well as the standard to stand for some time, usually over night, before final observations were made.

Of seven samples of hardened cottonseed oil examined, four samples contained 0.03 mg. of nickel in one kilo. One sample showed a relatively high content, 0.075 mg. of nickel; while the remaining samples contained 0.02 mg. of nickel. Palm kernel oil showed a content of nickel ranging from 0.017 to 0.1 mg. of nickel per kilo, averaging around 0.02 mg. Thus it will be noted that the nickel content of these fats is only about one-thousandth part of that found in foods prepared in nickel kettles, and when one considers that fats generally are not used for edible purposes, *by themselves*, but simply as additions to other foods, the amount of nickel furnished by hydrogenated fatty material amounts to so very little that the consumption of such food year in and year out may be regarded as harmless.

Even in fats intended for technical purposes, the amount of nickel is small as compared with that found in the food materials above mentioned, as for example:

	Nickel in one kilo
Hardened fish oil .....	3.3 mgs.
Hardened fish oil.....	1.2 mgs.
Hardened fish oil.....	3.2 mgs.
Hardened cottonseed oil.....	0.85 mgs.

**Meyerheim\*** notes that oils which are to be hardened for edible purposes should be washed with alkali to remove fatty acid in order to reduce the tendency to solution of nickel by the oil; also that care should be taken in filter pressing to completely eliminate the particles of nickel catalyzer.

The propriety of using, for edible purposes, low-grade fats which have been deodorized and cleansed by hydrogenation has been made the subject of considerable debate. **Bohm** states† that when Mege

\* Fortschr. Chem. Phys. and Phys. Chem., 1913, 305.

† Seifen. Ztg. (1912), 1087.

Mouries was working on the production of artificial butter it was far from his mind to use low-grade fats which had been purified by chemical treatment and that Boudet prescribed only fat of the best quality obtained from cattle slaughtered on the same day. Later when Huet claimed to make an edible product by thorough treatment of bad tallow with aluminium chloride solution, the margarine industry was hit a severe blow; for after such a proposal the opponents of artificial butter sought and with good results to prejudice the public against margarine.

Although to-day in a margarine establishment there is to be found the uttermost cleanliness as regards the plant, Bohm states that this is not true of the raw material before it comes into the hands of the margarine manufacturer. Even though, he declares, development of oil hardening may mean a great advance technically, it is coupled with such an opportunity for the employment of low-grade raw materials that it is likely to cause anxiety on the part of the public. In particular Bohm refers to the utilization of hardened fish oil in the margarine industry in which application technically it appears entirely suitable. Hardened fish oil, he states, is to be sure a chemically-changed, completely bacteria-free product; and physiologically is uninjurious. If, however, according to Bohm, we are to sanction the chemical treatment of fish oil, this would establish an important precedent for the application of all sorts of by-product fats and cadaver fats. When Hefter, together with other experts, formulated for the margarine industry the restriction that only those fats should be used which had been obtained from animals slaughtered under inspection, every consumer as well as every manufacturer of margarine was affected. With the inauguration of margarine manufacture from fish oil Bohm further states it appears not improbable that conflict with the present laws will arise.

Bohm refers to the assertion of Loock regarding *renovated* butter to the effect that no person who realizes the unpleasant properties of the original material would buy such butter, a statement, says Bohm, which can certainly apply equally well to whale oil margarine. Loock also cites a decision to the effect that no doubt exists that a food product is to be looked upon as unfitted for consumption when the raw material possesses a loathsome nature, irrespective as to whether the material through chemical treatment has been freed from such undesirable properties.

As to the loathsome nature of whale oil, Bohm asserts that one need only note the character of the methods employed in obtaining it in order to appreciate its undesirable nature. He maintains that a great part of the carcasses of whales are allowed to stand days at a time before they are worked up. Bohm indignantly declares the proposal to make an edible fat out of half-rotten whales which are treated in the hovels of the natives must naturally excite disgust. Perhaps, he says, a manufacturer of artificial butter may be able to use hardened fish oils in spite of the pure food laws, but may yet come into contact with the criminal courts, for when one buys margarine he expects to obtain freshly prepared beef fat and not a chemically-changed fish oil.

While this contention of Bohm may not be sound in some respects it is noted here for the sake of completeness. Naturally such an attack against a new and promising use for whale oil has not passed



unnoticed. See rejoinder by **Lieber** in *Seifensieder Zeitung* (1912), 1188, and editorial comment adverse to **Bohm**, also the opinion of **Keutgen**.\*

An oil which has been used so extensively by physicians all over the world as a remedial food for children **Lieber** believes cannot be looked upon as unsafe for human consumption. He calls attention to the hardy nature of the Eskimo whose principal or sole food is the blubber of the whale and seal. Furthermore, he contends that if the carcasses of whales were allowed to decompose, the oil which resulted would be of low grade and the pecuniary loss would be considerable. By the present system as soon as a whale is harpooned it is hoisted aboard the whaling ship and immediately rendered, the several grades of oil obtained being pumped to separate tanks. Every effort is made to produce the maximum yield of No. 0 and No. 1 oil because of the relatively high prices these bring.

Until seven years ago there was only a limited demand for whale oil, which was mainly used for the production of glycerine and fatty acids. It is now hydrogenated, for soap-making purposes, but in **Offerdahl's** opinion hardened whale oil is suitable for food. With regard to the traces of nickel present in the hardened oil, experiments showed that when small amounts of nickel powder were taken daily no ill effects were experienced, and that 99.8 per cent of the metal was rapidly excreted from the system. Hardened whale oils were found to be free from bacteria.†

The *Halbmonatsschrift f. d. Margarineindustrie* (Dusseldorf) discusses the question of the prohibition of the use of whale oil in the edible fat industry (*Seifen. Ztg.* (1914), 30) and from this discussion the following is noted,‡ — Ever since the discovery was made of preparing an odorless and tasteless fat from whale oil by the hardening process it has been taken for granted in those circles which are antagonistic to the further development of the margarine and artificial edible fat industry that hardened fish, seal or whale oil could be used in the preparation of butter substitutes. This suspicion was all the greater because of the increase in the last few years in the cost of most of the raw materials used in the margarine industry. It has been customary for the agricultural opponents of butter substitutes to condemn the raw products from which these products are obtained and in this way to seek to make this indispensable article of food repulsive to the consumer. But in recent years the knowledge that margarine practically does not influence the price of natural butter, and therefore does not enter into competition with it, has gained some little headway. Dr. Vieth, Director of the Dairy Station in Hameln (an authority in his line) has acknowledged this to be a fact. If the margarine does not

\* *Seifen. Ztg.* (1914), 89.

† *Offerdahl, Ber.* (1913), 558.

‡ See also the views of the *Deutsche Margarine Zeitschrift* (*Seifen. Ztg.* (1914), 118).

harm the butter industry, the bottom is taken out of the agitation which has been going on for over a decade against the manufacture of substitutes. In spite of this (*Molkerei Zeitung*, 1913) space has been lent anew to the suspicion that the raw materials used in the production of margarine cannot be entirely without effect.

Edible fats, such as hardened palm-kernel oil, cottonseed oil, etc., which have recently been introduced into the manufacture of margarine are thoroughly tested by government officials and scientific experts. The suspicion that infectious raw materials might be utilized can therefore apply only to the possible use of hardened whale and seal oil. In order, however, to prevent the spread of this idea and in order thereby to prevent a new danger to the butter substitute industry, the *Duesseldorfer Margarine Zeitschrift* suggests a legal prohibition of the use of whale oil in the edible fat industry.

It is supposed that the official foodstuff investigators will eventually aid this proposal. Its necessity is shown by the fact that an effort has been made from foreign countries to induce German margarine factories to use whale oil. The suggestion that well-known and reputable margarine factories have already started to use whale oil has been shown to be without foundation and is thought to be out of the question for the future. In order that no margarine made from whale oil may reach the German consumer because of unscrupulous manufacturers (and in that way the good name of a product which has been established only after many years of effort be brought into ill repute) but one remedy can be suggested: the prohibition of whale oil for food purposes. The trade journal of the margarine industry points out that such a value is placed by all classes of society upon margarine that the thought of utilizing any raw material repulsive to individual consumers ought to meet with vigorous opposition. It is evident from the editorial comment at the close of this article that the *Seifensieder Zeitung* is not in accord with the drastic views expressed in the foregoing.\*

On the subject of hydrogenated edible oils but little has appeared in the literature.† A number of patents discuss various products and methods of preparation.

An edible oil composition is described by Ellis ‡ comprising hydrogenated cottonseed oil and cocoanut oil, the mixture being beaten with air to improve the color of the product. The following formula and method of treatment are given: Ninety parts cottonseed oil are mixed with ten parts of cocoanut oil and the mixture subjected to the action of hydrogen at a temperature of from 150° to 160° C., in the presence of finely-divided nickel so as to convert a large proportion of the unsaturated into saturated material. A solid composition is produced which is then subjected to aeration which may be carried out by beating the hydrogenated product with rapidly revolving

\* Further comment by Keutgen on the same subject appears in *Seifen. Ztg.* (1914), 171.

† In an article on "Hydrogenated or Hardened Fat," appearing in the *National Provisioner*, Sept. 27, 1913, 104, Hall observes that hydrogenation is one of the greatest advances ever made in the fat and oil field.

‡ U. S. Patent 1,037,881, Sept. 10, 1912.

paddles until a sufficient quantity of air is incorporated in the product, in a finely-vesiculated condition to produce a material of the proper consistency and light colored appearance. Another statement \* gives details of a hydrogenated butter substitute in which various hydrogenated and normal oils are incorporated to make a fat approximating the melting point of butter, with which is mixed milk, etc., to produce a variety of margarine. These compositions should ordinarily have a melting point considerably less than the temperature of the human body, so that when the material is taken into the mouth, it immediately melts and does not leave a greasy sensation on the tongue and walls of the mouth. It is generally desirable to carry the hydrogenation treatment to a point where a product of rather firm consistency is secured. This produces a material, however, which is of too high a melting point for the production of a vegetable butter composition. Hence it is then pressed to remove the excessive amount of stearin. In the case of cottonseed oil, it is stated that it is desirable to hydrogenate until the iodine number falls to about 80. The oil may then be cooled to about 30° C., and allowed to stand for a time and pressed. Afterwards it is warmed to render it entirely fluid, and is incorporated with milk material. Suitable material of this character is ordinary full milk or skim milk or butter-milk, sterilized milk, sour milk or milk which has been specially fermented. Coloring material, such as ordinary butter color, may be added. Also a flavoring compound, such as cumarin and various esters and aldehydes, such as those of valerian and capryl bodies, may be added. In order to give the product the property of browning, when heated in a skillet, bodies such as egg yolk, milk sugar, lecithin or finely-powdered casein may be introduced.

A suitable oil base having been derived in this manner, the oily material is emulsified with the milk material to thoroughly mix the latter with the fatty body. For 100 parts of fatty material about 30 to 60 parts of full milk or perhaps 50 to 80 parts of skim milk are suitable proportions. In the summer months a stiffer composition is required than in the winter months and the fatty material should be compounded to give a material melting at the proper point with reference to seasonal temperatures. In emulsifying it is desirable to put a portion of the milk in the beating apparatus, and to stir for a short time. In the case of full milk, beating for 10 minutes or so causes a separation of the butter fat. The oil may then be added in portions, beating thoroughly until the composition is well incorporated. The remainder of the milk and fatty material may be added

\* Ellis, U. S. Patent 1,038,545, Sept. 17, 1912.

from time to time, and the temperature of the mixture should preferably be maintained between 30° and 40° C. When the composition has become thoroughly incorporated, it is run from the apparatus into a cooling device which cools the emulsified composition rapidly. It is then ready to be rolled and kneaded to remove the excess of water, etc., after which treatment the material is formed into the desired shape for shipment. The coloring material and salt and also flavoring material may be added during the emulsification process if desired.

The use of hardened oil in preparing oleomargarine compositions is the basis of French Patent 458,611, of 1913, to **Deveaux**.

Hydrogenated soya bean oil\* has been recommended, as well as hydrogenated vegetable oil and animal fats mixed to form lard-like products of varying composition. When employing cocoanut oil in such compositions it is desirable to hydrogenate it. To be sure, cocoanut oil usually has an iodine value of only 7 to 10, which is indicative of the small proportion of unsaturated bodies present. But, in spite of this, in order to secure a permanent product, which does not separate or grow lumpy on standing, and which remains in a perfectly neutral condition for a long period of time, even when exposed to the air, it is desirable that the iodine number of the cocoanut oil should be reduced to practically zero, if larger proportions than 30 per cent or thereabout are incorporated with hydrogenated soya bean or cottonseed oil.

An edible product of a superhydrogenated character † is obtained by carrying the degree of hydrogenation beyond the actual titer required and then pressing to remove some of the harder material so that the final titer of the expressed fat is that of lard, butter or whatever other titer may be required. Most oils of a vegetable nature and some animal oils contain from traces up to considerable quantities of highly-unsaturated bodies, including those of the linoleic and linolenic group. These and other similar bodies are very sensitive to oxidation and lend instability to edible oil products of this character by their tendency to change chemically and thus alter the flavor of the material. These bodies may be saturated by very careful hydrogenation up to the degree of consistency required in the edible product, but such hydrogenation is difficult to carry out commercially on a large scale with the assurance that the product will run uniform in quality. By saturating these bodies with hydrogen to an excessive degree as regards final consistency, these bodies lose their identity and become substantially free of odor of origin and tendency to rancid-

\* Ellis, U. S. Patent 1,047,013, Dec. 10, 1912.

† Ellis, U. S. Patent 1,058,738, April 15, 1913.

ify or otherwise be decomposed. By hydrogenating cottonseed or corn oil or similar oils to materially reduce the iodine number, the more sensitive double bonds are saturated with hydrogen and thereby eliminated and oxidation tendency is reduced to a minimum. Apparently the complete elimination of all the double bonds characteristic of the linoleic type is more difficult than the removal of the double bonds characteristic of the linolenic type, so that control over this seeming selective action during hydrogenation when saturating up to a given degree of consistency from a given oil is difficult, if not impossible, under ordinary conditions of hydrogenating. If, however, the oil is overhydrogenated so that a more consistent fat is acquired than is actually desired for an edible product, the unstable bodies thus may be completely transformed. In order to secure the degree of consistency desired the hot hydrogenated fat is gradually cooled to about 30° C., when the temperature may be maintained between 25° to 35° C., or so for several hours to induce crystallization or balling of the high melting point compounds. The mass is then pressed to the desired degree. Such a superhydrogenated pressed product which may be made either of butter-like or of lard-like consistency is stable in storage and is not liable to coagulate on standing with the formation of objectionable masses of granulous stearin-like bodies.

It has been noted when a vegetable oil such as cottonseed oil is hydrogenated directly until of the consistency desired that on cooling frequently it tends to granulate unless chilled or very rapidly cooled. This is objectionable in culinary operations as an initial lard-like body after once heating and slow cooling in the air often forms relatively hard granules of stearin-like bodies which look like little balls of coagulated material and separating as they do from the fluid oil under some circumstances give the product the appearance of having curdled or decomposed. By super-hydrogenating and pressing to the point required the granulating stearins or stearin-like bodies are eliminated to a greater or less extent and less easily crystallizing or non-granulating stiffening bodies remain tending from their amorphous texture to better maintain the original consistency and appearance of the product in repeated culinary use.

The **Boyce** process\* of producing an edible compound consists in preparing a mixture of synthetic stearin by the action of hydrogen in the presence of a catalyzer upon a previously unsaturated oil or fat, the latter being subjected to the catalytic action of hydrogen to a

\* Boyce, U. S. Patent 1,061,254, May, 6, 1913, assigned to the American Cotton Oil Co.

degree sufficient to convert the required fraction of the oil into synthetic stearin. The hydrogenation process is arrested at the point when the stearin is found to be present in the amount of about 20 per cent of the entire body of the oil. Boyce states that by arresting the action at this point there will remain a mixture of the unsaturated oil and the synthetic stearin produced by the hydrogenation of a portion of the oil.

A hydrogenated fatty food product containing hydrogenated corn oil has been described.\* When corn oil is suitably hydrogenated, a product is derived which has the property of improving the stability of hydrogenated cottonseed oil or similar hydrogenated oils which tend to granulate. Also it is stated that hydrogenated cocoanut oil may be used as a fluxing agent for chocolate in the manufacture of confectionery. The melting point of the fatty flux should preferably be about 90° to 100° F. Hydrogenated cocoanut oil olein may be used in a similar manner. The manufacture of the coating of chocolate creams calls for a relatively high melting point fat which incorporates readily with chocolate and does not impair its flavor. Cocoa butter is especially desired on this account, but is relatively expensive. Cocoanut oil melts so easily that in hot weather candies made with it soften very quickly when handled. Cocoanut oil also has a tendency to rancidify. By hydrogenation of an oil assimilable with chocolate the exact melting point desired may be obtained and a stable composition secured.

Hydrogenated oil of high titer, as stated, may be mixed with unhydrogenated oil to form a body of a consistency suitable for use as a substitute for lard. For example, hydrogenated cotton oil of a titer of say 52° C. (fatty acids) may be melted and incorporated with four times its weight or so of ordinary refined or deodorized cottonseed oil so as to form on cooling a white, opaque fatty material of the consistency of ordinary lard. The product made in this manner is not always sufficiently stable. Not infrequently in a short time it will lose its opacity to a considerable degree and will take on an appearance more suggestive of petrolatum than lard. Sometimes this change, which may be due to a tendency to form solid solutions of certain types, occurs irregularly in layers or isolated zones which give the product a curious mottled appearance, and this striated effect taking place in the containers during storage so changes the product, physically at least, that it is regarded as damaged or unfit for use by those accustomed to the normal appearance of lard. By disseminating through a fatty basis of a melting point and consistency approaching that of

\* Ellis, U. S. Patent 1,067,978, July 22, 1913.

lard, a quantity of fatty material of higher titer so as to form flocculations of a high titer product uniformly disseminated through the fatty basis, a product of better "color stability" is secured.\* The material of the relatively higher titer may be denominated the stabilizer and the proportions of fatty basis and stabilizer as well as their melting points and titers may be varied to meet various conditions of a climatic nature.

As an illustration one may take to make the fatty basis, 6 parts of hydrogenated cottonseed oil of a titer ranging between 52° to 54° C. (fatty acids) and 34 parts of refined and deodorized cottonseed oil. A thorough mixture is secured by the aid of heat and when well incorporated the melted product is chilled rapidly in a thin layer by feeding onto a chilled roll which is kept in constant rotation and from which the solidified product is removed in layers by a scraper. This product when properly set has a consistency approaching that of ordinary lard. The stabilizer is prepared by incorporating 3 parts of hydrogenated cottonseed oil of the same titer as that used in making the fatty basis, with 5 parts of refined and deodorized cottonseed oil. By heating the hardened oil with the deodorized oil the requisite mixture is obtained. As in making the fatty basis, the stabilizer is likewise chilled to form a solid, preferably in thin layers, and the two products are mixed in powerful mixing apparatus until the stabilizer is well disseminated through the fatty basis. To secure a desirable distribution both the fatty basis and the stabilizer may be fed onto the same chill roll in a series of adjacent or alternate streams, or the fatty basis may be allowed to fall on the chill roll, and when it has progressed a distance sufficient to solidify but not to stiffen it fully, the stabilizer is applied as a superposed coating adherent to and slightly intermingled at the contacting surfaces, with the fatty basis. This composite film is removed by the scraper and is then "pugged" or beaten. As the melting point of the stabilizer is preferably considerably higher than that of the fatty basis, the former congeals more quickly, so that although the superposed film is somewhat insulated from the chill roll by the fatty basis film yet the solidification of the upper layer is usually rapid enough to prevent material solution or interfusion of the two heterogeneous layers.

Further modifications are the following: Eighty parts of cottonseed oil are mixed with fifteen parts of hydrogenated oil of a titer of 48 (fatty acids). This is chilled and mixed with five parts of melted 42° C. titer hydrogenated or hard oil, or fat. Likewise one can superpose on a basis of 34 to 38 titer about 20 per cent of 40 to 42 titer. Cottonseed oil may be hydrogenated to 37 titer, chilled as described and similarly incorporated with about 10 to 20 per cent cottonseed oil hydrogenated to 40 to 42 titer. Thus there may be obtained a lard-like or otherwise consistent fatty material having its main titer to a considerable degree influenced so that the product may have the desired soft consistency of ordinary lard while actually containing bodies which if melted into the fatty basis would raise the melting point and consistency.

Palm oil, suitably hydrogenated, has been recommended for use in edible fat products.†

\* Ellis, U. S. Patent 1,070,331, Aug. 12, 1913.

† Ellis, U. S. Patent 1,087,161, Feb. 17, 1914.

The fatty acids of Kaya oil have been hydrogenated by Ueno (Chem. Rev. u. d. Fett. u. Harz. Ind. (1913), 209) who thereby obtained fatty acids melting at

Wilbuschewitsch \* regards his process as applicable to the treatment of all unsaturated acids and their glycerides, as well as for waxes and other alcoholic fatty substances. From castor oil there is obtained a product which melts at 83° C. The finished fat can be hydrolyzed and the fatty acids distilled. For example, from cottonseed oil there may be obtained fatty acids which melt up to 71° C. and make excellent candles. After suitable refining the products may yield satisfactory alimentary fats if the reduction is only carried so far that the melting point is between 28° and 34° C. Thus he finds from castor oil there may be made a product which is odorless and tasteless but retains the other properties of castor oil. So also from cod liver oil and other fish oils there may be made butter substitutes, or from vegetable oils substitutes for cocoa butter. Oils treated by the process lose their specific odor.†

It has been shown by Erlandsen, Fridricia and Elgstrom‡ that hardened whale oil is eminently suitable as a human food. Experiments were made with the whale fat in comparison with butter fat. The apparent digestibility ranges from 91.6 to 94.9 per cent for these two fats and the difference between butter and whale oil does not exceed 0.9 per cent. A margarine containing 22.8 per cent of the whale oil was used in an institution where 250 people were fed. A physician who was in constant attendance reported favorable results.

A sample of butter fat examined by Amberger§ contained only 2.4 per cent of triolein. By fractional crystallization of the glycerides of hydrogenated butter fat, it was found that the olein had not been converted into tristearin, but into a mixed glyceride. The greater part of the oleic acid in butter fat is therefore present as a mixed glyceride and not as triolein. Butyric and caproic acids are also present as mixed glycerides; tributyrin and tricaproin could not be isolated from the fat. Butyrodiolein, butyro- palmito-olein, and oleodipalmitin are present, as is shown by analysis of the glycerides isolated from the alcohol-soluble portion of hydrogenated butter fat. Amberger has also isolated another glyceride, m.pt. 67.9° C., from butter fat; this glyceride yielded a mixture of fatty acids, m.pt. 55.5° C. (See page 318.)

65.5° C. The hydrogenation of the material was carried out in alcohol solution using platinum black as a catalyzer. Kaya oil as employed for edible purposes is liquid and yellow in color.

\* U. S. Patent 1,024,758, April 30, 1912.

† The keeping properties of some hardened oils examined by Knapp (Analyst, 1913, 102) were found to be remarkably good. Although prepared nearly a year and a half previously, and having often been exposed to damp air, yet these samples showed no signs of rancidity. The acidity (0.7 per cent as oleic acid) did not appreciably change during the period of observation.

‡ Tidskrift Kem. 1918, 15, 109; Chem. Abs. 1918, 1793.

§ Z. Unters. Nahr. Genussm., 1918, 35, 313; J. S. C. I., 1918, 558A.



## CHAPTER XIV

### EDIBLE HYDROGENATED OILS—Continued

**Wesson** \* observes that one of the latest contributions of the chemist has been the hydrogenization of fatty oil which converts it into a solid fat by the introduction of hydrogen into the molecules of the unsaturated acids. This enables the manufacturer of cooking fats to turn out compounds consisting entirely of vegetable fat, which are fast displacing the mixtures of oil with animal fats formerly employed. By the new process of hydrogenation wholesome edible fats of the consistency of butter and lard are now produced entirely from what normally will probably continue to be our cheapest vegetable oil, namely, cottonseed oil.

**A. H. Gill** † discusses the subject of hardened oils in their various applications. Concerning edible products obtained by hydrogenation, he observes that

It is claimed for them that they can be heated hotter (to 455° F.) without smoking than ordinary fat: this cooks the outside of the food more quickly and prevents the grease from soaking in. Consequently it is less greasy, more digestible, dry and crisp. Another advantage is that no odor is absorbed; fish, onions and potatoes can be cooked successively in the same fat. Another claim is that one-fourth less is used of these fats than of butter; further that it is all fat, while butter contains 5 to 16 per cent of water.

Gill also notes that hydrogenated vegetable oils seem to offer a satisfactory substitute for animal fats to those who object to the latter from prejudice or religious scruples.

**Klimont** and **Mayer** ‡ consider the chief objections against the use of hydrogenated fish oil in the manufacture of margarine are that the production of the crude fish oil is not under proper control, that the disagreeable odor may reappear when the product is kept for a long time, that the hydrogenated oil may contain small quantities of nickel, and that it has a higher melting-point than any of the fats hitherto used for foods and hence would probably not be easily digested.

\* J. Ind. Eng. Chem., 1915, 277.

† Science Conspectus, Mass. Inst. Tech., 1915, Vol. V, No. 4.

‡ Z. angew. Chem., 1914, 27, 645; J. S. C. I., 1915, 148.

Klimont and Mayer were unable to detect nickel in hydrogenated oil examined by them; hence this test could not be relied upon for the detection of hardened fish oil in oleomargarine. The following test is proposed: 2 to 3 g. of the sample is melted, and dissolved in acetone to a total volume of 50 cc. After standing for twelve hours at the ordinary temperature, the crystals which separate then are filtered off, dried and weighed. Oleomargarine yields 12 to 13 per cent of crystals of M.P. 45° to 47° C. In the case of artificial mixtures of oleomargarine with hydrogenated fish oil and rape oil, the portion crystallizing from acetone was, in all cases, considerably greater than 12 to 16 per cent, which may be taken as the limits for genuine oleomargarine. It was possible by this test to detect 3.5 per cent of hardened fish oil when this was added, together with 5.5 per cent of rape oil, to oleomargarine.

Initially, Bontoux states, edible peanut, cotton, sesame and sunflower oil were hardened for use as edible fats in margarine manufacture but with the perfection of the hydrogenation process, lower grade oils including No. 0 and No. 1 whale oil were hardened.\*

A plea for the prohibition of hardened whale oil in oleomargarine is made by a number of German margarine concerns,† who base their petition on the inedible character of the original oil.

Bergius ‡ notes that a careful survey of the applicability of hardened fats for edible purposes fails to discover anything objectionable in such products.

The food value of hydrogenated oils has been studied by Pekelharing and Schut.§ White rats and mice, and a dog, were used in these experiments. The fats fed were hydrogenated whale, peanut, sesame and cottonseed oils. Frequent determinations of the fat content of the feces were made, and the general condition, changes in weight, etc., of the animals noted. The investigators conclude that these fats are not only harmless, but may well find application as human food and that they give best results when mixed with natural fats, as lard.

Thoms and Muller|| have made an extensive study of the chemical and physical properties and physiological action of peanut, cottonseed and other oils which have been altered by the hardening process so that they have a higher melting-point. Feeding experiments on man and animals indicate that they are harmless and are to be considered as useful articles of diet.

Holmes and Lang have published a paper entitled "Fats and

\* *Matières Grasses*, 1914, 4194; *Siefen. Ztg.*, 1914, 987.

† *Seifen. Ztg.*, 1914, 604; *Margarine Industrie*, 1914.

‡ *Seifen. Ztg.*, 1914, 728.

§ *Pharm. Weekblad*, 53, 789-85, 1916; *Chem. Abs.*, 1916, 2758.

|| *Arch. Hyg.*, 84, 56-77, 1915; *Chem. Abs.*, 1915, 1642.

their Economical Use in the Home,"\* in which they refer to the edible grades of hardened vegetable fats. They state that hardened oils used in this field are generally white in color, have no appreciable odor or taste and are less likely to become rancid than the original oil. They also state that a number of these fats marketed under a variety of trade names have proved popular and appear to be of quite wide application. It is observed that the hardening process may be of special value in the future utilization of some oils like fish oils which because of objectionable flavors or odors are not entirely suited for edible purposes in their natural state.

**Estabrook** † advocates a product for edible purposes, consisting of wheat flour mixed with comminuted hardened oil.

This product, when made into a dough by the addition of milk or water, and baked, is shortened by the presence of the hardened fatty material.

The shortening agent Estabrook states is made according to the following process: cottonseed oil is first heated and nickel salt is added thereto. Hydrogen is then conducted into the oil, and the heat is continued and mass the stirred constantly. The nickel salt acts as a catalyzer, causing the oleic acid of the oil to take up hydrogen, whereby it is changed into stearic acid. When the process of hydrogenation has progressed far enough to give the mass the desired hardness, which is ascertained by making a titre test, the melted fat is filtered off from the nickel and allowed to cool. The product thus obtained is stated to be much harder than natural hard fats, and due to the changes produced by the hydrogenation process it will keep for an indefinite length of time without becoming rancid. This, Estabrook explains, is due to the fact that the linolein of the oil, which tends to produce rancidity, is changed by the process into stearin. Freedom from rancidity he states is also due in a large measure to the fact that the hardened oil contains little or no olein, practically all of the oleic acid of the oil being converted to stearic acid by the process described; and any palmitin which may be present is unobjectionable for the reason that this is a solid and lends itself readily to the preparation of a dry-shortening flour.

The hardened oil is finely ground and mixed with flour. For the purpose of making biseuit or a similar product Estabrook states that about 12 lb. of the comminuted hardened oil should be mixed with 200 lb. of flour. The product may be sacked or barreled, for shipping purposes, and, as indicated above, may be kept for an indefinite length of time without material deterioration. Baking powder also may be added to the flour, as well as seasoning, so that for cooking purposes it is only necessary to make a dough of the product by adding milk or water, rolling it into a relatively thin mass and then cutting into biscuits and baking. For making pie crust, or similar types of pastry, Estabrook recommends the amount of hardened oil added to the flour to be about 24 lb. to 200 lb. of flour, and the leavening agent to be omitted. In making ordinary baker's bread the proportion is about 5 lb. of the comminuted hardened oil to 200 lb. of flour.

\* Bulletin No. 469, Department of Agriculture.

† J. S. C. I., 1914, 1218; U. S. Patent No. 1,117,012, November 10, 1914. See also Nos. 1,276,507, 1,276,508 and 1,276,509 issued August 20, 1918 to Ellis.

**Kohman, Godfrey and Ashe** employ hydrogenated fats in the manufacture of bread.\*

A shortening effect equal in value to that produced by relatively large quantities of liquid oil is stated to be obtained by the employment of a hard fat, which also permits the use of sufficient water not only to supply the amount required for giving stiffness and springiness to the dough, but to supply, in the baked loaf, the quantity recognized as desirable for imparting to the bread the expected freshness and flavor. The employment of the hard fat as the shortening agent is likewise found to add to the keeping qualities of the loaf, in the sense that even after the loaf has lost its original freshness, it lacks the rancidity frequently met with in ordinary bread which has been kept, under the same conditions, for the same period of time. For the present purpose they use as the shortening agent, a hard fat of either vegetable or animal origin,—as, for instance hydrogenated edible vegetable oil (hydrogenated cottonseed oil), hydrogenate, edible animal oil, or oleo-stearin. Kohman, Godfrey and Ashe give preference to the use of hydrogenated cottonseed oil, or other hydrogenated vegetable oil of an edible character, for the stated reason that such oils are relatively cheap, and can be hydrogenated or hardened up to a high melting-point readily and conveniently. Thus hardened cottonseed oil having a melting-point of 57° C. is well adapted for shortening purposes.

To incorporate the hard fat of high melting-point into the dough batch it is desirable to bring the former first into intimate admixture with flour. This may be effected by melting the hard fat and heating it somewhat above its melting-temperature and then mixing the flour therewith. The heating and mixing operation may be carried out in a rotary drum, having a heating jacket, and provided with stirrers. The temperature should be maintained, during the mixing operation, above the melting-point of the fat, so that the flour shall not chill the mass, or the flour may be preheated, for the same purpose. It is found that under these conditions a quantity of flour equal in weight to from 5 to 10 times the weight of the melted fat will absorb the fat, and that the flour will retain its pulverulent condition. The procedure involves heating only a relatively small quantity of the flour. Thus, if 1 lb. of hard fat is to be added to a dough batch containing 880 lb. of flour, it will suffice to absorb the fat in 5 to 10 lb. of flour, in the manner described, and it is found that in the subsequent mixing and kneading of the dough batch, the shortening thus added to the relatively small amount of flour will be uniformly distributed throughout the entire mass. This feature avoids heating the entire mass of flour up to the temperature of the small portion which has absorbed the fat.

The hard fat may also be incorporated with the flour in the manner following: The melted fat heated to a temperature of 200° C. and upward may be supplied from a suitable melting and heating receptacle to a discharge pipe from which it may be ejected, at a correspondingly high temperature, in the form of a fine spray or cloud, by a jet of air into an inclosed chamber. Into this chamber the flour may be sifted, and on coming in contact with the highly heated particles of fat sprayed into the chamber, take up the fat. The flour thus impregnated with the melted fat remains in a pulverulent condition, after cooling, and is available for use as a part of the flour ingredient of the dough batch. In

\* U. S. Patent Nos. 1,204,280 and 1,204,281, November 7, 1916.

this case it is found that by repeating the absorbing operation a number of times, upon the same body of flour a quantity of flour from five to ten times the weight of the fat is sufficient to absorb the fat and yet remain in a pulverulent condition.

It is found that, with equally good results as to color, texture and expansion, a quantity of the melted fat incorporated with the flour in either of the ways described may be employed of approximately one-twentieth the weight of the cottonseed oil used ordinarily in making up the dough batch. Thus, in those instances where from 2 to 3 per cent of cottonseed oil (calculated, by weight, on the amount of flour employed in the dough batch) was used, one-twentieth of that percentage, by weight, of hydrogenized cottonseed oil having a melting-point of 57° C. may be used, resulting, it is claimed, in like shortening effects with the production of a stiffer and springier dough; the viscosity of the dough being maintained, even though the absorption is increased, and the resultant baked loaf having an amount of moisture sufficient to give it satisfactory freshness and flavor.

Fats of a melting-point as low as about 35° C. can be used and the advantages incident to the use of the hard fats secured, although to a somewhat lesser degree than when the shortening agent consists of the higher melting fat without appreciable admixture of liquid fat. Even when fats of a melting-point as low as 35° C. are employed, the amount of the shortening agent in proportion to the flour of the bread is but a fraction of the amount of liquid shortening agent required for producing the same shortening effect and need not exceed 5 lb. of fat to 880 lb. of flour and bread. Fats of higher melting-point require a correspondingly less proportion by weight of fat to flour to produce the same shortening effect, and, when the melting-point of the fat approximates 57° C. the amount of the fat may be diminished to say 2 lb. of fat to 880 lb. of flour of the bread. In fact, the higher the melting-point of the fat, the less quantity, in proportion to the flour employed, will be required to obtain a baked loaf of satisfactory shortness, moisture-content and keeping qualities.

In a modification of the process of making a shortening composition \* **Kohman, Godfrey and Ashe**, heat flour to 200° C. or higher and atomize hydrogenated oil by means of a jet of air into the flour. To secure this admixture, the flour is sifted in at the top of a chamber into which the atomized oil is being introduced and on coming in contact with the colder particles of flour the hydrogenated fat is taken up by the flour. The latter remains in pulverulent condition after cooling. By repeating this absorbing operation a number of times upon the same body of flour, the latter will take up from one-tenth to one-fifth of its weight of the fatty material and yet remain in a pulverulent condition. As shortening material, this powder may be admixed with the requisite amount of flour and other materials used in making bread, thus introducing the shortening in a simple manner.

Hydrogenated oil in the form of a powder is suggested by **Atkin-**

\* U. S. Patent No. 1,242,883, and 1,242,884, October 9, 1917.

son \* as a shortener. Corn oil is hardened to a melting-point of about 148° F., and is ground in a mill having cooled rolls to give a fine powder. During the pulverization the temperature of the fat should be kept below its melting-point. The powder is stated to be particularly useful as a shortening composition for cereal baking products as it may be added to the flour or dough in definite quantities in lieu of lard, butter, or other solid or liquid shortening material and is more easily mixed with flour and dough than ordinary shortening fat or oil.

An edible product containing hydrogenated oil and carbohydrates in the form of a powder or as a solid cake is described by Ellis.†

A shortening and leavening composition employing hydrogenated oil is suggested by Holbrook‡ who finds it possible to incorporate the components of baking powder with thickened cottonseed oil to produce a composition which is stated to be stable and which, when mixed with flour and water to form dough, will serve both to shorten and leaven the mass.

The cottonseed oil is thickened to the desired consistency in any suitable manner, but, preferably, by partial hydrogenation or by mixing it with from 5 to 10 per cent of hydrogenated cottonseed oil. Such a fat, it is asserted, will not become rancid and does not, as an animal fat or lard appears to do, more readily acquire rancidity when admixed with leavening ingredients. The fat should be quite free from water, and baking powder or leavening materials, are intimately mixed therewith, either by stirring the leavening ingredients into the melted fat or mixing with the cold solid fat in a mixing machine. The fat and leavening materials are employed in such proportions that when the preparation is mixed with about eight parts by weight of flour and with sufficient water or milk to form dough and the mass baked, the product is properly shortened and leavened. Common salt for seasoning may be mixed into the preparation so that the baker need only add the composition to flour and water or milk to form the dough. Since the baking powder is embedded in the body of lard-like fat it does not easily absorb moisture from the air and hence retains its gas-producing capacity indefinitely. The baking results attained are said to be superior to those effected by separately mixing the shortening and baking powder in the dough in the ordinary manner. The explanation offered is that the baking powder ingredients are embedded in the shortening fat and the development of the leavening gas is, for that reason, diminished or retarded in the cold dough, and hence more of the leavening action occurs when the dough is exposed to the heat of the baking oven. For this reason also, the preparation is considered to be more economical since by its use a smaller amount of the leavening agent is required. Thus, if baking soda is used in the preparation as the source of the leavening gas, the amount needed to properly leaven a given quantity of flour is stated to be about 25 per cent less than is ordinarily required, and the amount of baking acid required to react with the soda is likewise reduced.

\* U. S. Patent No. 1,231,114, June 26, 1917.

† U. S. Patents Nos. 1,276,507, 1,276,508 and 1,276,509, August 20, 1918.

‡ U. S. Patent No. 1,210,940, January 2, 1917.

The leavening ingredients recommended are sodium bicarbonate and finely-pulverized acid phosphate such as mono-calcium or mono-sodium phosphate. Acid-phosphate, particularly mono-calcium and mono-sodium phosphate, are inexpensive and efficient baking acids, but they absorb atmospheric moisture and must, therefore, be especially prepared for use in ordinary baking powder. Thus, in a stable baking powder, mono-calcium phosphate should be used in granular form (i.e., such that it will not pass through a 156-mesh sieve), rather than in pulverulent form (i.e., such as would pass through a 200-mesh sieve). But, since the leavening ingredients are embedded in a body of shortening fat, finely-pulverulent acid phosphates can be employed in Holbrook's preparation without detriment to its keeping qualities and with advantage in the baking results attained. Like the acid phosphate, the sodium bicarbonate and salt employed may be finely pulverized and dried.

In preparing the composition, the materials and proportions by weight are, for example, as follows:

Thickened cottonseed oil.....	7 parts	Mono-calcium phosphate ..	1 25 parts
Sodium bicarbonate.....	1 part	Salt.....	1 part

The leavening and seasoning ingredients are dried, finely pulverized and intimately mixed with the thickened cottonseed oil either in the hot or cold state. The proportions given are such that 1 part by weight of the improved preparation will be sufficient to properly shorten and leaven dough containing 8 parts by weight of flour, which is stated to be the proportion in which common animal shortening fat or lard is generally used.

**Burchanal** \* prepares a food compound closely simulating lard in its physical and chemical characteristics, consisting of a mixture of an oil and a hardening agent produced by hydrogenizing an oil or liquid fat.

In its most desirable form, the product is a vegetable one, consisting of a mixture of about 85 per cent of cottonseed oil and 15 per cent of hydrogenized cottonseed oil. In the manufacture of this product, oil is hydrogenized, by vigorous agitation in a closed vessel containing an atmosphere of compressed hydrogen, a catalytic agent, such as kieselguhr impregnated with finely-divided nickel, being maintained in suspension in the oil and the charge being heated to a temperature of about 155° C. The oil is thereby converted into a white or yellowish solid, containing additional hydrogen about 5 to 6 per cent more than in the nonhydrogenized material, having a saponification value of about 190, an iodine value of about 20, a melting-point of about 56° C., and a titre of about 55° C., giving no reaction for cottonseed oil under the Halphen test. Suitable proportions of the hydrogenized and hardened oil and of the non-hydrogenized oil are now thoroughly mixed or blended. In case about 15 per cent of hydrogenized cottonseed oil and 85 per cent of non-hydrogenized cottonseed oil are thus mixed, the final product is stated to be a white or yellowish semi-solid, having a saponification value of about 195; an iodine value of about 95; a melting-point of about 42° C.; and a titre of about 36° C.

In case a harder hydrogenized stock is used, its proportion may be correspondingly reduced. For example, if the oil used for hardening is hydrogenized

\* U. S. Patent No. 1,135,935, April 13, 1915.

to an iodine value of 8 or 9, approximately 10 per cent of the hardened material are stated to be required to yield a mixture having physical constants approximately as above specified.

**Burchanal** \* produces an incompletely hydrogenated lard-like fat from cottonseed oil, with the stated object of providing a new food for a shortening in cooking, in which the liability to become rancid is minimized, and in which the components of such vegetable oils which are inferior and detrimental to use as such a food product have been, to a large extent, converted into a higher and more wholesome form.

All such vegetable oils contain glycerides of unsaturated fatty acids, and among these, notable quantities of fatty glycerides of lower saturation than olein. Oxidation is largely the cause of rancidity, which oxidation weakens the fat at the point of absorption at the double bonds, and these glycerides of lesser saturation readily absorb oxygen from the air at ordinary temperatures, while the more highly saturated glycerides, as olein, only absorb oxygen at elevated temperatures. It is evident, Burchanal observes, that oils or fats containing notable quantities of glycerides of linolic acid, or of lesser saturation, are distinctly inferior as an edible product to those containing a minimum of these glycerides with a larger per cent of olein. On the other hand, while it is important to get rid of the readily oxidizable glycerides of lower saturation it is also important not to supply too large a per cent of fully saturated glycerides. The saturated glycerides of the arachidic, stearic, palmitic and other groups are stated to be of very small value for shortening, inasmuch as it is the liquid fats which contribute this value to the material. Saturated fats, however, serve the purpose of congealing the shortening within the food, and thus retain it equally distributed throughout the whole. Oil, liquid at the ordinary temperatures is not regarded as making the best shortening, because the oil remains liquid, keeping the food in a soggy condition, and the oil will even settle to the under part of the cooked product. Moreover, fats of a melting-point above the temperature of the human body, 98° F., are not so digestible as fats which are liquid at this point, or which have a melting-point below 98° F. Burchanal therefore endeavors to change the chemical composition of the oil (cottonseed) to obtain a product with a high percentage of olein, a low percentage of linolin and the lesser saturated fats, and with only sufficient stearine to make the product congeal at ordinary temperatures.

Hydrogenation is, therefore, stopped when the oil has been converted into a product which cools to a white or yellowish semi-solid resembling lard. In many respects, it is claimed, the product is superior to the best leaf lard as a shortening. It is not so liable to become rancid and the product can be heated to a considerably higher temperature than lard without smoking or burning. The high temperature to which the product can be raised without smoking or burning is stated to make the product ideal for frying as a crust forms almost instantly on the food fried, which prevents any absorption of the shortening. Burchanal gives data on the analytical constants of the product. A lard-like product thus prepared from cottonseed oil has a saponification value of about

\* U. S. Patent No. 1,135,351, April 13, 1915.



195; and an iodine value ranging from about 55 to about 80. The product having an iodine number of 55 has a titre of about 42° and a melting-point of about 40° C.; that having an iodine value of 80 has a titre of about 35° and a melting-point of about 33° C. While but partially hydrogenized, containing from about 1.5 per cent to 2.5 per cent of additional hydrogen more than in the non-hydrogenized material, it shows no free cottonseed oil when subjected to the Halphen test. It contains from 20 to 25 per cent of the fully saturated glycerides, from 5 to 10 per cent linolin and from 65 to 75 per cent olein, and an average of a number of samples gives 23 per cent of saturated fats, 7.5 per cent linolin and 69.5 per cent olein, while the cottonseed oil before treatment contained 37 per cent linolin and 46 per cent olein.

Walker\* proposes a method of making fatty food products which consist in partially hydrogenating unsaturated compounds of vegetable or animal oils and fats, by any method and arresting the operation at a predetermined point short of saturation and where the consistency of the product is above or below that of a given oil or fatty body, and then incorporating with the partially hydrogenated body an unhydrogenated oil or fatty body to produce a product of the desired consistency and having the characteristic flavor desired. For example, purified cottonseed oil is hydrogenated until the action reaches a point where the stearine produced amounts to about 22 per cent of the oil treated, there remaining about 80 per cent of unsaturated oil. These proportions may vary with wide limits, depending on the consistency of the final product desired and the nature of the subsequent additions. To the hydrogenated product freed from catalyzer, oily lard is added, preferably by means of incorporating rolls, the quantity being sufficient to give to the hydrogenated product a lard consistency.

The process is stated to be equally applicable to making butter substitutes, the manufacture of coatings for chocolate creams, confections and the like.

Walker considers it is important that the hydrogenating action be carried to a point affording a consistency above or below that of the final product, and then to secure the desired consistency by incorporation of a suitable oil or solid fatty body, thereby securing the benefits of the added body as a hardening or softening agent while retaining its desirable flavoring characteristics unimpaired. In general, the hydrogenating action may vary between a product which is soft and greasy to a solid, but for the preparation of lard and butter substitutes the hydrogenating action should afford a product containing about 18 to 22 per cent of stearine.

\* U. S. Patent No. 1,206,954, December 5, 1916.

At the Institute of Hygiene in Wurzburg, the Director, **K. B. Lehmann** has busied himself with the question of the edibility of hardened oil\* and in particular to answer the questions: (1) In the hardening process does the fat take up quantities of nickel which would be injurious? (2) Does the product exhibit any abnormal characteristics as viewed from the chemical standpoint? and (3) How well fitted is the hardened fat for human consumption as evidenced by the effects produced by it on animals and on men when taken as an article of diet?

An analysis of several samples of hardened oils showed that nickel was present in amounts ranging from 0.1 milligram to 6 milligrams per kilogram of fat. In cottonseed oil, for example the amount of nickel present was about 0.5 milligram per kilo. This means that in 2,000,000 parts of the fat, but one part of nickel is present. Lehmann has shown that food prepared in nickel vessels contains from 11 to 64 milligrams of nickel per kilo and that by the use of such nickel vessels in the preparation of foodstuffs as much as 117 milligrams of nickel may be consumed in a day's ration. In a series of tests made with animals, from 6 to 10 milligrams of nickel per kilogram body weight of the animal, were fed for a period of 200 days without injurious effects. In tests made on man, up to 1 to 2 milligrams of nickel per kilogram body weight were consumed without injury. No case has been reported of acute or chronic nickel poisoning due to the general use of nickel vessels in the household for the preparation of food. Assuming the extreme case of a consumption of 100 g. per day of hardened fat, the content of nickel in this amount of fat would be 0.6 of a milligram when taking the fat having the maximum per cent of nickel. Under ordinary conditions the amount of nickel would be about 0.1 of a milligram per day, which, in comparison with the possibility of consuming over 100 milligrams of nickel per day in food cooked in nickel-coated vessels, is indeed a wholly insignificant amount.

A chemical examination of the hardened fat (prepared from peanut, sesame and cottonseed oil) did not disclose anything prejudicial from the hygienic standpoint.

After having secured these results from the ingestion of nickel and finding that no injurious effects were detectable when nickel in vastly larger amounts than found in hardened fat was daily consumed, Lehmann directed his attention to the continued action of the hardened fat itself, first on animals and then on man.

For a period of five months, 50 g. of the fat were daily fed to dogs of body weight 4 to 8 kilograms and the suitability of the fat as a foodstuff determined from this standpoint. The results were entirely favorable. Lehmann then began a series of tests of the fat on members of his own and other families. In three families 7 lb. of hardened fat per month were used over a period of several months duration without any ill results. In his own family the product has been used regularly for six months and no criticism can be found against the fat. In summarizing his work, Lehmann concludes from theoretical and practical investigations that hardened fat is a most rational and desirable fatty

\* Chem. Ztg., 1914. 798.

food and regards it as a most valuable material to use in the production of oleomargarine.

**Vuk** offers,\* as a partial explanation of the divergent views of various authorities concerning the harmful effects arising from the use of nickel utensils for cooking and containing foods, certain results showing that various forms of nickel are dissolved by dilute acids with different degrees of facility.

By heating separate portions of 700 cc. of 5 per cent acetic acid for 2½ hours on a water-bath together with each of the different kinds of nickel of which exactly 16,800 sq. mm. were exposed to the action of the acid in each case, the following amounts of nickel were found to have been dissolved, results being expressed in mg. of nickel per sq. dm. of surface: Rolled 15.5-16.9, cast 25.5-28.8, electrolytic 30.6-30.8, drawn 33.1-39.0, and Berndorf "Rein Nickel" 61.4-65.4.

As regards the use of nickelware in the preparation of food **Gheorghiu** † boiled ordinary salt pickles and meat with water and salt two hours in a nickel dish, the resulting products (pickles, liquid, fat and meat) were examined for metal with the following results: pickles 107.4 mg., juice 135.6 mg., fat 16 mg., and meat 0.0 mg. per kg. substance.

An edible product comprising edible fatty hydrogenated material free from catalytic metal is mentioned in U. S. Patent to **Ellis** No. 1,097,308, May 19, 1914.

A method of increasing the glycerine content of oils and fats is recommended by **Naamlooze Vennootschap Ant. Jurgens Vereenigde Fabrieken** ‡ which consists in heating the fatty material with glycerine in the presence of a finely-divided metal oxide, such as alumina, thoria or titanium oxide. It is supposed that bodies of this character exert a catalytic action under these conditions. By the treatment, the triglyceride is converted to a greater or less degree into mono- or diglyceride. Glycerine enrichment has been found to improve the flavor of many oils, such as cod liver and castor oil.

From cottonseed oil a product containing a considerable proportion of diglyceride was prepared as follows:

One hundred parts cottonseed oil, 10 parts glycerine and 3 parts alumina were heated for one hour at 250° in an enamelled receptacle fitted with a mechanical stirrer. To avoid oxidation a slow current of hydrogen was passed through the apparatus. At the end of three hours the excess of glycerine was removed by washing with water.

Before such treatment, the oil exhibited a saponification value of 189 corresponding to a glycerine content of 10.3 per cent. The acetyl number was 12. After the treatment, a portion of the oil was acetylated and 1 g. of the acetylated product was saponified, calling for 263.5 milligram potassium hydrate.

\* *Z. Nahr.-Genussm.* 28, 103-4 1914; *Chem. Abs.*, 1915, 109.

† *Ber. pharm. Ges.*, 24, 303, 1914; *Chem. Abs.*, 1915, 487.

‡ *Seifen. Ztg.*, 1914, 1092; German Patent No. 277,641, May 26, 1914.

From this is deducted the acetyl value found, leaving 251.5 milligrams potassium hydrate, corresponding to the total hydroxyl groups of the glycerine present. This is equivalent to 13.75 per cent of glycerine or 3.45 per cent more than was present in the original oil. If calculated to diglyceride, the content of the latter would amount to 66 per cent. In another test, 100 parts sesame oil, 12 parts glycerine and 10 parts comminuted kieselguhr were heated to 230° under conditions similar to those employed with the cotton oil. After heating for three hours, the product was cooled and washed with warm water.

Saponification value of the original oil.....	191.2
Glycerine content corresponding.....	10.5
Acetyl number.....	11.5
After treatment and acetylation 1 g. oil required...	259.9 ing. KOH
Deducting acetyl number.....	11 5
	<hr/>
	284.4

This result corresponds to a glycerine content of 13.59 per cent equivalent to 60 per cent diglyceride.

It is stated that the formation of glyceride by heating fatty acids and glycerine is already known as also the fact that mono- or diglycerides form on heating a triglyceride with glycerine. The use of a contact body to enable the reaction on triglycerides to be effected expeditiously at temperatures between 200° to 250° is the indicated improvement.

A pamphlet entitled "The Present and Future Peril to Our Commerce and Industry," by **Dr. Hugo Schweitzer**, discusses the development of methods of converting waste into edible fats. Schweitzer states: "Germany imported from us (U. S.) altogether \$23,000,000 worth of fats, principally lard, for culinary purposes. The interference with our seaborne commerce through the action of the British Navy has suspended our trade with Germany in this commodity."

"Fortunately for Germany, but unfortunately for us, a modern development in the fat and oil industry has provided her with means to utilize materials which hitherto were unfit to eat.

"By the so-called method of hardening fats and oils—that is, by treating them with hydrogen—they are not only converted from the cheaper liquid into the higher-priced solid form, but their taste and odor are so improved that they might serve for culinary purposes, while without being subjected to the hardening process, they could not possibly be thus employed. Even the various grades of fish oil can thus be rendered available as food materials. Germany cannot possibly be cut off from the supply of these oils. The fisheries of the Baltic and the North Sea, of Norway and Sweden would place an inexhaustible and cheap source of fats and oils at the disposal of the German people, to whom an opportunity is thus afforded to remain forever independent of the import of edible fats from the United States.

"By this hardening process even the waste fats (foots) obtained in refining can be utilized not only for soap making, but also for foodstuffs. In short, by

suitable treatment with hydrogen, all oleaginous matter may be converted into edible substances." \*

#### UTILIZATION OF FISH OIL

It is reported by *J. Ind. & Eng. Chem.* (1918, 487) that authorities in Germany have prohibited the supply of herrings to the trade except with the heads removed in order that these may be utilized for the production of oil, albumen and phosphate of lime. Fish offal is now utilized in Germany to produce food for human beings as well as for animals. Offal collected from fish preserving factories, restaurants, etc., is dried and, after the extraction of the oil, ground. The meal so obtained frequently contains 50 per cent and upwards of albumen and phosphate of lime, the latter being obtained from the bones and heads. By chemical methods, the albumen is extracted from the fish meal and rendered available for human consumption. From the oil phosphate of lime for animal fodder is obtained by means of benzene, benzol, and other fat solvents. The oil is also used for various technical purposes. Specially good kinds can be hardened by hydrogenation and rendered suitable for production of eatable fat. The hardened fat looks like tallow and is almost odorless.†

After determining that corn oil is an economic substitute for olive oil, **Dean L. E. Sayre**, of the Kansas University School of Pharmacy, Lawrence, Kan., is reported by the *Soap Gazette & Perfumer* (1915, 99) to be experimenting to determine whether it is a satisfactory substitute for lard. Some of the liquid oil, which is heavy and brown, was hydrogenated. In this condition it appeared white and about the consistency of cocoa butter, and melted at the temperature of beeswax. Dean Sayre believes that the hydrogenated oil can be used in place of lard, the dietetic value of the oil being claimed to be as great as that of either olive oil or cottonseed oil. The patented frying mediums are stated to be hydrogenated cottonseed oil.‡

The **Proctor & Gamble Company** have erected, at Hamilton, Ontario, a plant for the manufacture of Crisco, and will also operate glycerine and cottonseed oil refineries for their Canadian trade. The Crisco building is similar in construction to their Ivorydale factory, the inner walls being of white glazed brick, the air circulation undergoing a constant process of purification.§

A method of purifying hydrogenated fats is described by **Joslin**.¶

It is stated that hydrogenated fats contain fatty acids and other bodies which effect the taste and odor and also certain readily oxidizable components which may be removed by treatment with denatured alcohol or wood spirits. A volume of alcohol approximately equal to the volume of the fat taken is agitated

\* From an address delivered before the German University League, New York City, February 3, 1915.

† **Leimdorfer** refers to the fat-hardening process in connection with the edible field. *Seifen. Ztg.*, 1915, 344.

‡ See also **Luckey** and **Sayre**, *J. Am. Pharm. Assoc.* 6, 348.

§ *Amer. Perfumer*, 1915, 104; *Soap Gazette*, 1915, 224.

¶ U. S. Patent No. 1,152,023, August 31, 1915.

with the latter while maintaining the mixture in a fluid condition. As low a temperature as is possible is employed, in fact, just sufficient to maintain the proper degree of fluidity of the fat. A small amount of alcohol, ordinarily from 3 to 5 per cent, dissolves in the fat while the impurities and objectionable substances dissolve in the alcohol. The alcohol with the dissolved substances is removed by decantation and the alcohol taken up by the fat is removed by distillation. This step is preferably followed by a further treatment consisting in passing steam or inert gas through the fat. The refined substance is allowed to cool in an atmosphere of inert gas. In some cases more than one treatment with alcohol may be required to secure the required degree of purification. The purified hydrogenated fat is stated to be characterized by containing a relatively inappreciable proportion of free fatty acids and a relatively large proportion of combined fatty acids, and by being free from impurities, unsaponifiable bodies, rancidity-tending oxidized products or other bodies of an unstable nature.

For refining hydrogenated fats to produce edible products, **Wilbuschewitsch** \* removes the fatty acids by saponification successively

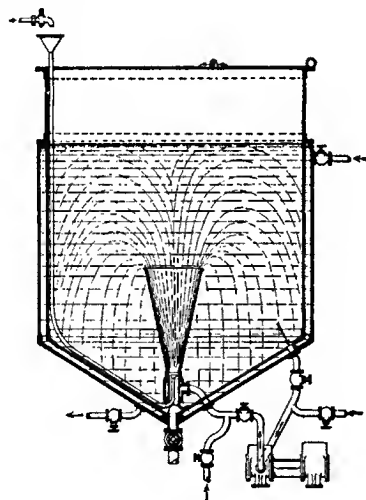


FIG. 54a.

with carbonate of soda and caustic soda, subsequently removing the soap and washing the oil thoroughly, then deodorizing with superheated steam in a vacuum apparatus. Fig. 54a illustrates apparatus in which the oil and alkali are mixed by a circulating pump.

A statement by **Oelwerke Germania** in *Seifensieder Zeitung*, 1914, 208, regarding the **Leprince and Siveke** patent of 1902 is as follows:

Hence it follows as a matter of fact that the process of German Patent No.

\* U. S. Patent No. 1,177,911, April 4, 1916.

141,029 made a new path in the industry and first solved the important problem of oil hardening. No one before this had thought of the possibility of making a solid edible fat from oils. This information is first supplied by Patent No. 141,029.

The properties and uses of various hardened oils are referred to by **Thompson,\*** who states his impressions of the industry as viewed in 1914. A comparison of conditions at that time with those prevailing since the present world war began is interesting.

The total cost of the hardening operation differs widely in different places, and varies some with the degree of hardness to be produced. It is said to average around 1 cent per pound. In some places it has been done for a commercial toll of 1½ cents, which presumably leaves a profit.

The combined capacity of the hydrogenating plants of Europe is estimated for 1914 at 250,000 tons (1,375,000 barrels), which is two or three times as much as has ever been treated. These plants are in England, Norway, Germany and France, and are engaged at present chiefly on fats for soap and candles. They are hardening linseed, whale, soya bean and cottonseed oils.

The great increase in the demand for margarin in Europe, for compound lard in the United States and for hard soap all over the civilized world has resulted in closely crowding the supply of natural lard fats, while liquid oils are relatively abundant. A few years ago strictly edible liquid oils seemed to be growing scarcer, but the new scheme of deodorization began to relieve this shortage by lifting the so-called soap oils into the edible class. The same process was applied to copra and palm-kernel oils, and finally caused a scarcity of soap greases. Hydrogenation now promises a further readjustment of conditions by permitting the transfer at will of any oil from the liquid to the solid class, and it will bring into use some relatively rare oils and encourage the production of still others.

#### LINSEED OIL. (THOMPSON)

Linseed oil, in 1914, offered the greatest attraction to hardeners. The price in Liverpool in April, 1914, was 5.40 cents per pound, or 2 cents cheaper than average tallow. It is now successfully hardened and used for soap on a large scale, 750,000 barrels being the trade prediction for 1914.

The world's crop of linseed varies greatly from year to year. In 1913 there was a record crop of about 2,700,000 metric tons, or half a million above that of the year before. Omitting the crush of Russia, which is about 350,000 tons out of a crop of 500,000, Europe crushed linseed in the last two years as follows:

	1912. Metric Tons.	1913. Metric Tons.
Germany.....	324,700	560,000
United Kingdom.....	290,000	665,400
Netherlands.....	156,600	207,600
Others.....	235,000	266,700
Totals.....	1,006,300	1,700,000
Oil made (estimated 30 per cent)...	301,890	510,000
Equivalent, barrels.....	1,660,000	2,805,000

\*Special Agents Series, Bureau of Foreign and Domestic Commerce; Oil, Paint and Drug Reporter, October 19, 1914. 36.

Seventy per cent increase in the oil supply had a depressing influence on the market and caused the price to decline through the year in the face of a general advance for other fats. This fact no doubt had its weight in accelerating the development of hardening plants. The crop for 1914 is expected to be smaller, about like that of 1912; and if so, this extra demand, together with the growing demand from the linoleum industry, will tend to advance prices.

#### FISH OILS. (THOMPSON)

Fish oils (whale, seal, menhaden, sardine, etc.), have generally ruled lower in price than vegetable oils, because of their restricted uses. They have not been successfully used in the manufacture of soap because of the persistent smell. It is claimed that the new hardening process eliminates all trace of smell and taste and renders these oils as useful and valuable as tallow for soap. It is even claimed that they may be used in margarine. Whale oil has advanced a cent or two per pound on this news, but is still only about 5 cents against 7 to 8 for tallow. One large hardening plant has already been established in Norway (De Nordske Fabrik Fredrikstad), principally for treating whale oil, and another plant is also being built. The combined capacity of these two plants is estimated at 550,000 barrels for 1914. Other plants in Germany and England are also working on fish oils. This has greatly stimulated the whaling industry, 800,000 barrels being estimated as the catch for 1913, which is many times greater than any previous year. Although new whaling fields are continually being exploited, extinction of the species is predicted if the present activity continues.

Oils are being extracted in relatively small quantities at various fishing centers in England, Japan, South Africa and other countries. When there happens to be a surplus catch beyond the capacity of the local market they are worked for oil instead of, as formerly, being thrown out on the land or worked whole into commercial fertilizers. The introduction of steam trawlers in England has enlarged the fishing radius with a consequent increase of catch. The new outlet for fish oil will help to absorb the surplus and prevent an economic waste.

#### SOYA BEAN OIL. (THOMPSON)

From the present crop of two or two and a half million tons of soya beans could be made two million barrels of oil, but no such amount is being made, or at least offered to commerce. Only 200,000 to 250,000 barrels are made in Europe, and any amount greatly in excess of this would have to move as oil from China and Japan. As this oil is now definitely moving in the direction of salad, and as that trade must draw a supply from somewhere, the probabilities are that in the end it will be allowed to go that way and not much of it be intercepted for hardening.

#### PEANUT AND COTTONSEED OILS. (THOMPSON)

Peanut oil is so much esteemed in liquid form for salad and for margarin that there will not be so much margin of profit in hardening it as for some of the others, and it will probably be left for exploitation at a later date.

Oil from Egyptian cottonseed, say 374,000 barrels made in Germany and England, is all tending toward the edible trade, though about half of it, natural or hardened, still goes into soap. Eventually most of it will probably go into



compound lard and margarin, perhaps in the hardened state, especially as it is claimed that the hardening process also deodorizes.

Oil from American decorticated cottonseed, three to three and a half million barrels, is now practically all turned to edible uses, and its value will be much enhanced by the new discovery. Either hardened in the United States or shipped abroad to be hardened for margarin and compound lard, it becomes an immediate competitor of copra oil, the highest-priced ingredient on the market. American oil will always have the preference, because it exists in the largest amount, thus presenting the largest possibility for selecting a uniform supply. Reversing the usual order, increased domestic demand for the new form will absorb such quantities that export prices may be maintained at high levels.

Thompson \* observes that formerly artificial lard was made by the admixture of bleached liquid cottonseed oil with oleo stock or refined tallow in the right proportion to give a consistency as nearly like lard as possible. But since the introduction of the hardening process, much of the artificial lard is made by mixing liquid oil with hardened cottonseed oil. Margarine, or artificial butter is in general compounded from the same kind of fats as used for artificial lard. Natural hard fats are more difficult to obtain and higher in price than liquid oils, so the artificially hardened fats have become immensely popular for all these mixtures, even whale oil having been used during the war.

A liquid hydrogenated oil food product is described by Lowenstein † which is stated to be suitable for use as a salad oil, cooking oil or for such other purposes as cottonseed oil, or similar oils have been used, the product being superior to such oils in keeping qualities.

A further advantage of the new product lies in the fact that the dissolved stearin therein is found to crystallize most readily, which quality renders the product especially suitable for winter or cold pressing for salad oil. Accompanying cottonseed oil or other fatty oils, notably seed oils, are always certain impurities. According to Lewkowitsch (Technology of Oils and Fats) "these can be removed for the most part by steaming or washing with water, followed by bleaching or filtering, but even after this purification small quantities of non-glyceridic substances remain dissolved. Some of these must be regarded as entirely foreign substances, e.g., traces of coloring matter, chromo genetic substances (producing the color reactions which are characteristic of some oils and fats)." While refined choice or prime yellow cottonseed oil keeps very well in dry storage, bleached or bleached and deodorized cottonseed oil (produced by steaming) does not keep so well under similar storage conditions but tends to become rancid very much more quickly than the refined undeodorized yellow oil. Cottonseed oil which has been partially hydrogenated, does not exhibit this tendency toward rancidity even though bleached oil is employed. Nor does the hydrogenated oil, if subsequently deodorized, develop this tendency. In other words, hydrogenation as carried out in the manufacture of the new product appears to have so altered or destroyed the non-glyceridic substances present that the oil has been markedly improved as to its keeping qualities. That there has been such a change in the quantity or character of the non-

\* J. S. C. I., 1918, 166 R.

† U. S. Patent No. 1,187,999, June 20, 1916.

glyceridic substances is evidenced by the fact that the product does not respond to the Halphen test, which is characteristic of cottonseed oil.

In carrying out the process for the manufacture of the product, a fatty oil, for instance choice or prime yellow cottonseed oil, is placed in a closed vessel and caused to be chemically combined with hydrogen in the presence of a catalyzer. A temperature of 150° to 200° C. has been satisfactorily employed and the time required to produce the desired result after attaining this temperature is from five to thirty minutes, depending upon the activity and proportion of the catalyzer employed.

Depending upon the particular cottonseed oil treated by the process the iodine value of the finished product varies from about 90 to 102. Its titre (as determined by the Wolfbauer method) has been slightly increased during the process to the extent of from about  $\frac{1}{10}$ ° C. to  $\frac{5}{10}$ ° C. over that of the original oil treated. The color of the treated product is usually somewhat lighter than the original oil. On cooling the product it in part readily crystallizes, thereby making the separation of stearine from the oil much easier and more effective for "winter pressing" for salad oil than is the case with ordinary cottonseed oil. The product responds negatively to the Milliau test for cottonseed oil.

**Brauer** \* notes that both laboratory experiments and those made on a commercial scale indicate that hardened fats have a much greater capacity for "holding" water than untreated fats, and that the same is true of margarines made from the two kinds of fats. Margarines made of (a) hardened whale oil and unhardened linseed oil (b) hardened linseed oil mixed with unhardened oil, and (c) tallow and unhardened linseed oil, contained 25.67 per cent, 18.33 per cent and 11.75 per cent, respectively, of moisture.

The fat-soluble accessory growth substances of beef fat and "oleo-oil" are considered important food elements by **Halliburton** and **Drummond**.† Margarines containing these bodies are nutritively equivalent to butter. On the other hand it is asserted that coconut oil, cottonseed oil, peanut oil and hydrogenated vegetable oils contain little or none of these accessory substances and that margarines prepared from these are not equal to butter in nutritive value.

The introduction of hydrogenated products in margarine manufacture according to **Clayton** ‡ marks a great technical advance, and one which is likely to develop very rapidly in the future. He observes that an objection has been raised by **Brauer** that hardened oils raise the moisture content of a margarine, owing to their property of retaining water, much in excess of what other oils do. **Brauer** claims to have proved this on a large scale on many occasions.

\* Z. offent. Chem., 22, 209; Chem. Zentr., 1916, II, 527; Chem. Abs., 1917, 1699; Zeitsch. angew. Chem., 1916, 29, Ref. 492; J. S. C. I., 1917, 98.

† Journal of Physiology, 1917, 51, 235-251. J. Chem. Soc., 1917, 112, i, 673. J. S. C. I., 1917, 1285.

‡ J. S. C. I., 1917, 1205.

Clayton notes that as far as he is aware such a difficulty has not been met with in British factories, and in any case the problem admits of very easy solution. The use of hardened oils really hinges upon their edibility or otherwise, and on this point much controversy has raged. Little doubt exists as to their being thoroughly suitable for human consumption, since they are assimilated during human metabolism just the same as any other fats, but whether the traces of metal catalyst almost invariably present affect the health, was, for a long time, a dubious matter. Another objection that has been raised against the use of these oils in margarine manufacture, is that good products may be prepared from bad raw material. As a particular instance, whale oil can be hydrogenated to yield a tasteless, odorless, and germ-free fat, physiologically harmless. Suspicion was aroused that margarine manufacturers might use cheap and unwholesome fish or other oils, hardened to form good, clean products. Much controversy has centered round this point. So long as the raw material was unsound, the public would not sanction the final margarine. Maybe, Clayton adds, there will be a legal fixing of the raw material in the future. At any rate, such a course has been frequently advocated, especially in the United States.

The utility of hydrogenated oils in the manufacture of oleomargarine receives further confirmation by **Pickard**,\* who states that for the purpose hydrogenated or hardened oils are used in considerable quantities. He further states that when the process is properly handled, the melting-point of the resulting material can be regulated to a nicety and the oils contain no appreciable amounts of deleterious substances, so that they are, therefore, perfectly wholesome and, in consequence, legitimate constituents of edible products.

**Keebler** states that the principal difficulty experienced with some manufacturers of nut margarine is that of keeping the melting-point above 75° F., while butter melts about 92° F. However, it is claimed by one manufacturer that his nut margarine has a melting-point of 107° F. Keebler observes that this possibly can be accounted for by the use of hydrogenated oils.

In the manufacture of leavened bread it is the practice to add various milk products to improve the flavor, etc. The addition of milk tends to retard fermentation by yeast and **Kohman**, **Godfrey** and **Asche** ‡ have found that by peptonizing the milk the fermentation is accelerated rather than retarded.

\* American Food Journal, 1918, 16.

† Am. Food Jour., 1918, 363.

‡ U. S. Patent No. 1,222,304, April 10, 1917.

In addition to milk they find that various forms of cheese may be employed and that it is preferable to mix the cheese with a hydrogenated fat such as hydrogenated cottonseed oil having a melting-point of about 35° to 40° C. A creamy mixture is obtained by incorporating these ingredients and such mixture may be readily introduced into the dough batch during the usual mixing operation. The addition of the hardened fat to the cheese is desirable for the further reason that the fat replaces a part or all of the shortening agents that are ordinarily added to bread. Ten parts of cheese to 4 or 5 parts of the hardened fat may be employed and 1 to 1½ lb. of this mixture may be used to 100 lb. of flour.

A product called *Vegetole*, manufactured by Armour & Co., according to the *American Food Journal*, June, 1917, page 330, is a hydrogenated cottonseed oil, without flavor and fully sterilized. It is stated that *Vegetole* differs slightly from lard and also mixtures of cottonseed oil and oleostearine and that it also has different properties from cottonseed oil. It is observed that the hydrogenated oils form a class by themselves and bid fair to constitute a most important part of what are known as cooking fats. *Vegetole* is sweet, wholesome and nutritious and easily digested and can be used for all purposes for which lard is used. As a shortening agent, whether in bread, pie crust, or biscuits, or when used as a medium for frying, the results obtained are stated to be excellent.

According to **Bernegau**,\* fresh white of egg is treated at about 40° C. with freshly expressed pineapple juice (containing yeast cells), and the resulting liquid mixed with sugar, emulsified with fresh egg yolk, and sterilized by heating, yielding an emulsion suitable for blending with hydrogenated oils to produce an edible fat.

**Poulenc Frères** † claim that the hydrogenation of lecithin may be accomplished by the aid of common metals and their oxides, and at a temperature below that at which lecithin and hydrolecithin are decomposed, by having the catalyst in its most active condition, obtained by slow reduction in the case of the metals and by dehydration of the hydroxides at a low temperature in the case of the oxides; by vigorous stirring of the lecithin so as to expose continually fresh surface to the action of the hydrogen, and by working under increased pressure.

**Daughters** ‡ hydrogenated oil from the seed of the wild cucumber (iodine No. 117) using a nickel catalyzer and a temperature of 220° to 240° C. The hydrogenated product melted at 29° to 36° C. and had an iodine number of 76.6. Feeding experiments with mice showed that the original oil and the hydrogenated fat were non-poisonous.

\* German Patent No. 295,351, March 24, 1914.

† French Patent No. 478,193, July 22, 1914; J. S. C. I., 1916, 1131.

‡ J. Ind. Eng. Chem., 1918, 126.

## CHAPTER XV

### USES OF HYDROGENATED OILS AND THEIR UTILIZATION IN SOAP MAKING

#### USES OF HYDROGENATED OILS

Liquid fats and fatty acids are essentially cheaper than solid fats and fatty acids, and the ability to prepare from ordinary *liquid* fatty oils a fatty body of almost any desired degree of consistency or hardness renders hydrogenation especially attractive in the production of edible fats and soap-making materials. These are, undoubtedly, two of the most important applications, although hydrogenated oils are likely to have a rather wide use in the arts. In the manufacture of insulating compositions and lubricants, for example, the hydrogenated fats may be used to advantage. In the tanning industry the stearin produced by hydrogenation is being used as a substitute for oleo-stearin.

The physical and chemical properties \* of hardened oils, particularly the hardened fish oils, indicate that these products are useful in the manufacture of lubricants and that they may be used as a substitute for tallow in the preparation of various lubricating compounds.† In compounding preparations of this character, the requisite amount of hardened oil is added to the oil base employed, the mixture being heated to secure satisfactory incorporation, and then is cooled, when it is ready for use. The better grades of hardened fish oil also can be used alone as a substitute for acid-free machine tallow.

A review of the soap trade of the United Kingdom for 1913 is significant in indicating decreased requirements of several of the staple raw materials, which condition, rather than suggestive of any decline in the production of soap, marks a greater dependence upon supplies which have been brought within practical operation largely through the hydrogenating process for hardening oils. To quote from the report on this subject:

"It is of the greatest moment that the European soap maker has found in the hardened oils produced by the hydrogen process very considerable relief from factors that must have driven values very much higher, had not this new source of supply come into actual operation."

\* Seifen. Ztg. (1912), 1092.

† Hydrogenated fats, Leimdorfer states (Seifen. Ztg. (1913), 1317), can be used in the preparation of lubricants and in tanning operations.

"English manufacturers as a rule are quick to turn to advantage any opportunity to exploit new methods and processes in their industries, and the recognition of the practical application of hydrogenated oils in such an important field as soap making is a development of much interest to the affected trades in this country, where the process in its general relationship to the soap and lard compound industries is in a more or less experimental stage. According to the English soap trade report the losses in three of the leading materials available for home consumption, as measured by the excess of imports over exports in 1913, were 3532 tons of tallow, 1656 tons of palm oil and 2240 tons of cocoanut oil. Exports of soap from the United Kingdom last year were heavier (1732 tons), while imports from foreign countries were lighter by 2194 tons. As a result of the strides in the hardening of materials for soap production by hydrogenation, whale and linseed oils are now accorded an established place in the Kingdom's soap industry. The total capacity of the hardening plants in Europe, including the United Kingdom, is given as 220,000 tons of oil, although some of the views expressed in the local trade place it to 300,000 tons. A good part of the American linseed oil export trade last year has been attributed to the heavier requirements for the soap kettle through the hydrogenation process, and crushers and dealers have been buoyed to keener expectations for this year's foreign business. Conditions in other fields in which linseed oil enters must, however, be reckoned upon as contributing factors. Persistent attempts have been made to induce our soap makers to adapt hardened linseed oil to their service, and while sales of round parcels have been made for this account, so far as is known none of the purchasers has been encouraged to put the oil into actual test. The favorable market conditions for competing fats in the soap field may have accounted for the attitude of makers toward linseed oil for this particular purpose."

"Probably the greatest headway in the application of the hydrogenating hardening process in this country has been in the field of edible products in which cottonseed oil has entered on the most liberal scale. It was through this means that the domestic consumption of refined oil during the last crop year so surpassed the general expectations of the trade that the principal markets abroad were scoured last summer to reclaim any supplies of our oil that might be available, and foreign producing sources were also called upon to help relieve the stringency here."\*

Auerbach† considers the hydrogenation process responsible for an advance in the price of fish oils so that they will be of doubtful benefit to the soap industry. Also he states that the so-called burned odor which was noticeable in soap made from hardened fats is said to have been overcome. Besides fish and whale oil, he notes that castor oil is treated to some extent. The hardened castor oil is used for insulation purposes in the electrical field.

#### HYDROGENATED OILS IN THE SOAP INDUSTRY

The developments in oil hydrogenation have brought to the soap industry an innovation of fundamental importance in the domain of raw materials. The soap manufacturer, no longer well able to purchase the best grade of fats in face of the high prices paid by the margarine and other edible fat industries, has now at his disposal the

\* Oil, Paint and Drug Rep., Feb. 2, 1914.

† Chem. Ztg., 37, 297.

means for utilizing lower grade materials in substitution for more costly stock.

By hydrogenation, oils which formerly made soaps only of soft consistency, now yield the more valuable hard soaps. This has led to a very rapid development of the art with respect to the production of soap-making fats. In particular, fish and whale oils have been made use of, because these oils may be completely deodorized by the addition of hydrogen.

According to a Japanese chemist, Tsujimoto, the odor of fish oil is due almost entirely to a fatty constituent and not to so-called impurities. This fatty constituent is elupanodonic acid having the formula  $C_{18}H_{28}O_2$ , which, therefore, by the addition of 8 hydrogen atoms, becomes stearic acid. When hydrogenated down to an iodine number of about 50, fish oil has the consistency of hard tallow and the odor of fish oil is wholly absent. Even the fishy taste is scarcely in evidence.

For soap making this product is satisfactory as it complies with the test for a deodorized fish oil suitable for soap making in that the odor of the original oil is not apparent when ironing laundered goods on which such soaps are used. If, however, at least with the poorer grades of oil, the hydrogenation is not carried on to a point where the iodine number is approximately 50 or less, there is some danger that the fishy odor will become apparent during the ironing operation.

It appears not improbable that unstable odor-forming nitrogenous impurities in fish oil add hydrogen during the hardening process and are transformed into bodies of a stable character.

Data on a hydrogenating plant in Norway is furnished by Commercial Agent E. W. Thompson of the Department of Commerce (Consular & Trade Reports, Jan. 14, 1914, 171) who reports that during the summer of 1913 an oil-hardening plant was opened at Fredrikstad by De Nordiske Fabriker, with head office at Christiania.\* The original object was to harden whale oil for the soap industry, but as the result of experiments with edible oils the plant is being enlarged to a capacity of 1000 barrels a day with the expectation of hardening cottonseed and peanut oils for the margarine makers. If this plan is successful it may double the

\* This concern is said to be a German-Norwegian company, capitalized at about \$833,500, organized to work a new German method of hydrogenation. The Hafslund Falls are being utilized to generate the electric power required by the work and also to manufacture by electrolysis the hydrogen required for the hardening process to which the purified whale oil is submitted and converted into a solid neutral fat. The daily consumption of oil is about 300 barrels. (Jour. Ind. and Eng. Chem. (1913), 608.) The hardened fat has a melting point between 40° to 50° C. and is stated to be odorless and tasteless. Although at the present time principally used for soap making, in all probability in due course the material will be employed in the manufacture of edible fats. (Seifen. Ztg. (1913), 1413.)

consumption of cottonseed oil in the margarine industry. The Norwegian firm will purchase the best grades of cottonseed and peanut oils, and will also harden on toll. Many European margarine factories are experimenting on hardened cotton and peanut oils to replace copra oil, which is high in price.\*

Some criticism has been directed at the use of hardened oils at least for edible purposes on the ground that nickel is used in the process, but the manufacturers say that although nickel is generally used none of it is left in the oil, and that even if it were it is harmless, as shown by many tests with animals and with human "poison squads."

Samples of Norwegian hydrogenated whale oil which have come to the author's attention are of exceptionally high quality.

Whale oil of the grades known as 0 and 1 hydrogenate readily with nickel as a catalyzer. No. 2 is somewhat more difficult and No. 3 is decidedly troublesome to treat without special refining.

Chinese wood or tung oil may be rendered very hard by thorough hydrogenation and the product often shows the property of expanding on solidifying from a melted state, forming a friable mass instead of a firm block. Hardened linseed oil sometimes exhibits a like behavior.

Hardened chrysalis oil is described by Tsujimoto (Jour. Chem. Ind. Tokio, 1914, No. 191 and Chem. Ztg. Rep. 1914, 110). Hydrogenation was carried out with a nickel catalyzer and traces of nickel were found in the ash of the hardened product.

Soya bean oil has become an important raw material for hydrogenation purposes. (Seifen. Ztg., 1914, 348.)

The commercial side of fat hardening is discussed to some extent by Schicht † and the value of fish and whale oils in this field is considered. The probable place hardened fats will assume in the soap and edible fat industry is discussed in *Seifensieder Zeitung* (1913, 768).

In this country very little has as yet appeared in the literature regarding the application of hydrogenated oils in soap making, but in Germany considerable space has been given by the trade journals to discussions of the subject. Some of the statements are of a very contradictory character as is, of course, to be expected in the early stages of development of this important subject, especially in view of the very considerable degree of empiricism which prevails in some branches of the soap-making industry.

It is to be regretted that so much of the published matter relates to products offered under trade names such as Talgol, Candelite and

\* Hardened sunflower oil is mentioned in *Seifensieder Zeitung* (1913), 611. The Knowles Oxygen Company, of Wolverhampton, England, has contracted with the Sunlight Soap Factory, in Port Arthur, to erect an annex to the plant for the production of the hydrogen necessary for hardening palm oil; the oxygen is to be collected and sold.

† *Seifen. Ztg.* (1913), 287.



similar hydrogenated fish and whale oils, etc., of the Germania Oelwerke at Emmerieh, but while soap making as practiced in Germany differs in several respects from the practice in this country, it is believed the work abroad will prove at least suggestive if not instructive.\*

In the following an attempt has been made to briefly review the more important contributions in this connection.

Garth † states that fish and whale oils are the raw materials for a considerable proportion of the hydrogenated products which, up to the present time, have found application in soap making. Being relatively low-priced raw material many attempts have been made to make cheap soaps from fish oil. These attempts in the past have been unproductive because the objectionable odor reappears after goods are laundered. Hence there are many proposals directed toward the production of odorless fish oil. As is known fish oil contains nitrogenous compounds and certain of the lower fatty acids arising from decomposition of the fish before the oil is expressed. Most of the proposals are based upon the assumption that these sources of the evil odor can be removed by the action of energetically-reacting bodies such as sulfuric acid and the like. However, neither treatment with strong acids nor distillation with superheated steam produce unobjectionable products. By hydrogenation the disagreeable odor disappears; nevertheless, there always remains an odor similar to that of distilled olein which, however, is completely concealed if the product is worked up with a goodly proportion of other fats.

Garth ‡ observes that the hydrogenated fats which have been used in the soap manufacture appear in the trade as Talgol, Talgol extra, Candelite, Candelite extra, Crutolein, Talgin, etc. Talgol has a melting point of 35° to 37° C., and an iodine number of 65 to 70. Talgol extra melts at 42° to 44° C. and the iodine number is 45 to 55. The Candelite products are harder, Candelite melting at

\* In England one large concern is offering several grades of hardened fat ranging as follows:

	Iodine No.	M. P.	Titer
A1 .....	50	40-42	36
A2 .....	85	28-30	32
C1 .....	60	44-46	45
C2 .....	75	35-37	36

† Seifen. Ztg. (1912), 1278.

‡ Seifen. Ztg. (1912), 1279.

48° to 50° C., and having an iodine number of 15 to 20, while Candelite extra melts at 50° to 52° C. and exhibits an iodine number of 5 to 10.\*

Heller † furnishes the following data on these products:

	Acid No.	Saponification No.	Unsaponifiable	Iodine No.
Talgol.....	3.5	190.7	0.33	63.9
Talgol extra.....	3.8	190.5	0.31	36.1
Candelite.....	3.8	190.4	0.41	18.4
Candelite extra.....	4.4	188.4	0.52	10.4

## FATTY ACIDS

	Melting point	Titer	Acid No.
Talgol.....	38.5	34.6	199.7
Talgol extra.....	45.5	43.5	199.9
Candelite.....	48.5	47.4	198.9
Candelite extra.....	51.8	50.5	199.9

Schaal has reported ‡ the results of his observations on the two products Talgol and Candelite derived by hydrogenation of fish oil, etc., and has called attention to the adaptability of these hardened fats in the production of soap base or milled soap. Both Talgol and Candelite have a tallowy appearance with this difference, that one is softer and one is harder than tallow. At first glance one is likely to regard these fats as similar to high-grade soap tallow, but the odor of the product immediately shows this is not the case. The odor is not disagreeable and in fact resembles some grades of tallow. It is suggestive of the cheesy odor given off by tallow which has been stored for a considerable time in warm weather. Of the two products Talgol and Candelite, the odor in the latter is less noticeable.

In his first investigations Schaal simply replaced a part of the softer fats, as he thought Talgol would lose its firm consistency during the

\* The Ölwerke Germania has trademarked in the German Patent Office the words Andelite, Candolit, Cancellit, Coryphol, Doratol, Dural, Durettol, Durohit, Durotin, Durotal, Duru, Durutol, Jutol, Jutolin, Kandel, Kandelin, Kandetil, Kanderit, Kerzenit, Kritolit, Krunotin, Krutello, Krutol, Krutolin, Talgela, Talgelin, Talgol and Urutol. (Taschenkalender f. d. Oel und Fett Industrie, 1914.)

† Seifenfabrikant (1912), No. 31.

‡ The results of investigations by Schaal on the utilization of hardened oils in soap manufacture are published in the Seifensieder Zeitung (1912), 821, 846, 954 and 979; (1913), 173, and in a book entitled Die Moderne Toiletteseifen-Fabrikation, Augsburg, 1913, to which reference should be had for detailed description.

boiling operation and would return to a consistency approaching that of the original oil. This assumption proved to be unwarranted as tests with small samples showed that the Talgol fatty acids were as hard as the Talgol itself. The first fat mixture used for preparing a soap consisted of the following:

40 parts tallow.  
15 parts Talgol.  
30 parts bone fat.  
15 parts coconut oil.

No rosin was used as it was desired to determine the influence of the Talgol odor. During the boiling the odor of Talgol was plainly in evidence, much more noticeable in fact than could be observed afterwards in the finished soap. The dried curd exhibited a wholly agreeable odor in which the characteristic odor of Talgol could not be detected, and no odor was in evidence of a nature calculated to affect the perfume. The soap was not perfumed, but was wrapped in paper and laid aside a few weeks for further observation. In another trial the tallow was reduced and the Talgol increased in amount, the formula being:

25 parts tallow.  
35 parts Talgol.  
30 parts bone fat.  
10 parts coconut oil.

The saponification progressed satisfactorily, indicating that Talgol readily united with alkali. As the bone fat employed was of exceptionally dark color, the soap was bleached in the kettle with 0.2 per cent Blankit. The dried product had a fine ivory white appearance, but the odor of Talgol was apparent although not so pronounced as to render the soap unusable. This soap base milled very smoothly and easily, giving an excellent finish. In another trial 5 per cent of rosin was introduced with improvement in the odor of the soap base.

The milled and perfumed soap was kept under observation and it was noted that some perfumes were affected by the Talgol odor. A person with a keen sense of smell would immediately detect the presence of Talgol. Tests were conducted with a number of perfumes\* including hyacinth, lilac, rose, pathouly and violet, each cake being separately wrapped in parchment paper. It was found that the two first-mentioned perfumes were more sensitive to the presence of Talgol smell and gave a momentary impression that the soap had become

\* Schaal gives a number of perfume formulae for hydrogenated oil soaps in *Seifen. Ztg.* (1912), 979.

rancid; the rose was slightly affected while the other samples were not noticeably changed. Schaal reaches the conclusion that the highest grade of toilet soap perfumed with delicate essential oils is affected by the use of Talgol or Candelite and that these hardened oils will not find an application here. Such soaps are, however, sold only to very fastidious trade and require in any case perfumes of the very highest grade. On the other hand, in manufacturing ordinary grades of toilet soap which are, of course, made in enormous quantities, up to about 35 per cent of Talgol or Candelite may be employed advantageously in the fat stock. As regards solubility in water and free lathering properties, Schaal found Talgol or Candelite to afford satisfactory results, the soaps which he prepared forming a lather immediately which was thick and voluminous, acting in fact like any standard soap. It is reported that the Ölwerke Germania has been successful in producing a completely odorless product at a somewhat higher cost. If such a deodorized product can be put out at reasonable price, it will be possible to make toilet soaps of the highest grade with hardened fats derived from relatively cheap oils.

Of Talgol, Schaal notes that the fat is readily deprived of its glycerine and especially well by the Krebitz process,\* and soaps made from this stock are prime products.

Schaal states that so long as these hardened fats are not entirely odorless, as indicated they cannot be advanced for the manufacture of soap stock of the first class. For these, the best beef tallow, etc., must remain the raw material, for this class demands the best that the soap industry can produce. Talgol is therefore considered suitable only for working up into soap stock of second and third grade. In these soaps the price of raw material plays a considerable rôle, and thus Talgol proves an advantageous substitute for tallow. Pure Talgol soap has too little lathering power and as its odor is also objectionable it is not advisable to allow the addition of Talgol to rise above 40 per cent. The lathering power will be considerably better if 10 per cent of palm kernel or cocoanut oil is worked in and the solubility of the soap is also much increased. If, however, 60 per cent of other fats are present, bad lathering is prevented, and the product meets the requirements of the trade. The yield of pure salted soap on the average is 165 per cent.

The following are some recipes given by Schaal for soap stock of two grades.

\* The Krebitz process is recommended for the treatment of hardened fats in the manufacture of toilet soaps. (Seifen. Ztg., 1914, 391.)

*Soap Stock, Second Grade*

- |                              |                              |
|------------------------------|------------------------------|
| (1) 30 parts Talgol extra;   | (2) 40 parts Talgol extra;   |
| 40 parts beef tallow;        | 25 parts beef tallow;        |
| 15 parts peanut or corn oil; | 20 parts peanut or corn oil; |
| 15 parts cocoanut oil.       | 15 parts cocoanut oil.       |

*Soap Stock, Third Grade*

- |                               |                               |
|-------------------------------|-------------------------------|
| (1) 40 parts Talgol extra;    | (2) 40 parts Talgol extra;    |
| 15 parts beef tallow;         | 30 parts oleomargarine waste, |
| 30 parts oleomargarine waste, | bone fat, hide fat, etc.;     |
| bone fat, hide fat, etc.;     | 20 parts bleached palm oil;   |
| 10 parts palm kernel oil or   | 6 parts cocoanut oil;         |
| cocoanut oil;                 | 4 parts rosin.                |
| 5 parts rosin.                |                               |

It may be noted that with each increase in the amount of Talgol, a similar increase in the amount of softer fats is demanded. Talgol extra is a rather hard fat and easily permits a considerable addition of fluid fats, producing a pliable plastic soap base which can be easily milled. Talgol like tallow is saponifiable with some difficulty and for the complete combination of it with alkali, boiling for a number of hours is required. The boil must be conducted with weak lyes of 15 to 20 degrees in order to get a good combination of fat and lye. With respect to the odor of the soap it is an advantage if the reaction between the fat and lye is extended over as long a period as possible, since the odor of Talgol thus almost completely disappears. When possible the Talgol material should be well blown with steam in the kettles, as by this treatment the odor is almost completely removed.

The resulting soap base displays absolutely no difference from that of a straight tallow stock, and works up on the machines exactly as a soap from beef tallow; indeed it may be said that milled soap from Talgol has a finer, cleaner and whiter look than that made without it. The odor may be permanently concealed in finishing the soap by means of appropriate perfumes.

The tests made by Schaal of Talgol as a constituent of cold process soaps led to the conclusion that it only has value in combination with cocoanut oil. The saponification of Talgol may be accomplished with strong tepid lyes if the following conditions are observed. First the temperature of the fat at the moment of contact with the lye must be at least 50° C. and on cold days about 55° C. It is desirable to warm the lye to 25° to 30° C. before incorporating. It often happens on mixing that the whole mass suddenly solidifies so that the mixture must be warmed to liquefy. Even when the temperature of the bath is higher than the figures given, solidification takes place

on running in the cold lye, or at least small lumps are formed. The union of the fat and lye takes place very quickly; the mass becomes solid in a short time and can be framed. On this account the frames must be ready at hand. In the frames a rather strong reaction sets in, and heat is generated. The frames should be well covered to take advantage of this rise in temperature. The finished soap is very hard and almost brittle in character and on this account must be cut while fresh. It has a fine white color, but is not transparent. The odor is not unpleasant, and varies with the fat used; it can be completely covered by oil of citronella or lavender. Artificial oil of bitter almonds is less adapted to permanently cover the Talgol odor.

The following is a useful formula:

25 parts Talgol,  
25 parts Ceylon cocoanut oil,  
5 parts castor oil,  
28 parts caustic soda lye, 37° Be.

The mixture of fats at a temperature of 45° to 50° C. is stirred well with the lye, which need not be warmed. In about one-half hour reaction is under way and the product should at once be framed. If delayed longer, the mass becomes almost in a moment solid and must be warmed to soften. This is unnecessary if the frames are ready at hand as above cautioned. This soap heats up strongly in the frames and on cooling is plastic with a somewhat transparent look. It lathers freely like a shaving soap and when properly perfumed is an excellent product. Such a soap is well adapted for pressing, which gives it a fine solid appearance.

For cocoanut oil soaps which are to be filled, 25 per cent of Talgol is recommended. Such soaps cut and press well and have a good solid feel. The batch should be maintained at a temperature of 40° C. when stirring, lest the soap get too solid before the filling is worked in. If this temperature is maintained no trouble need be feared with the lye or the filling. In weighing off the oil it is to be noted that the cocoanut oil should be first introduced and then the Talgol. Otherwise the latter sticks to the side of the kettle and the entire mixture then has to be made hotter than is necessary. 75 per cent of filling can be incorporated with 25 per cent of Talgol, giving a yield of 225 per cent without danger that the filling will settle out or fail to be held up. The soap is moulded as soon as thick and the moulds left covered for two hours. The cooled soap is hard and tenacious but still may be readily pressed. For filling, any desired solution of salt, potash and sugar in water may be employed.

The following is an appropriate recipe for a soap of this class:

22½ kilos Ceylon cocoanut oil,  
7½ kilos Talgol,  
16½ kilos caustic soda lye, 37° Be.,  
22½ kilos filling solution,

perfumed with 200 grams of oil of citronella or 200 grams of lavender or 100 grams of each oil.

For soaps with more than 75 per cent filling and yields of 250 per cent and over it is best to conduct the process in the warm way.

A cold process shaving soap made from 80 per cent Talgol extra and 20 per cent cocoanut oil exhibited satisfactory lathering properties, but in spite of strong perfuming the Talgol odor eventually reappeared, especially at the surface of the cakes.\*

In a discussion of available substitutes for palm kernel oil † it is stated that hardened fish or whale oil such as Talgol cannot be used as a substitute for palm kernel oil. The peculiar musty odor of Talgol, which to be sure no longer resembles that of the original oil, is, however, decidedly penetrating. Several grades of soap made with Talgol and Crutolein yielded a soap of too pronounced an odor to be marketable. Soap containing these hardened products was made into a soap powder and although the percentage of the hardened fat in this product was low, its presence was still detectable by the odor. It is, however, stated that if means can be found for the removal of this characteristic odor, the situation as regards the general utility of these hardened fats will be entirely altered.‡

\* Weber, Seifen. Ztg. (1913), 421.

† Seifen. Ztg. (1913), 312.

‡ Neither tallow, palm kernel or cocoanut oil can be completely substituted in soap making by hardened fish or whale oil, but the latter may be used to advantage as an addition fat in laundry soaps. (Seifenfabrikant (1913), 30; Zeitsch. f. ang. Chem. (1913), 310.)

Leimdorfer (Seifen. Ztg. (1913), 284 and 310) treats of hardened fats with special reference to the soap industry.

The addition of hardened oil to other soap stocks is advantageous for lowering costs and gives a satisfactory product when not used to excess. When caustic potash is used for saponifying a mixture of 65 per cent cottonseed oil and 35 per cent Candelite the soap does not grain but remains clear. (Seifenfabr., 33, 30.)

§ Hardened oils have faced several problems. The technician at first looked upon them with distrust. The peculiar odor of these fats has caused considerable criticism and their surprisingly white color has been looked upon as unnatural. The soap produced with this stock has a characteristic structure and its appearance changes somewhat in storage. The distrust evidenced toward hydrogenated fat is shown, however, to be unjustified.

Hardened oils when used in soaps\* in the proportion of 50 to 80 per cent give products which are very hard, dissolve with difficulty and do not lather readily. The saponification is also said to be somewhat slower than with ordinary soap fats. When about 30 per cent of hardened oil is used the soap is satisfactory.

Semi-boiled soaps were made as follows:

(1) 50 parts each of cocoanut oil and hardened oil were saponified at 80° C. with 38 degree caustic soda lye. The lye was stirred into the hot oil mixture and the kettle kept covered until a well saponified product was obtained. A little alkali was added to show a faint excess alkali by phenol phthalein. After short standing the soap was framed and cooled. It had a fine white color, but possessed a sharp odor (which however can be diminished or removed by boiling). The lathering qualities appeared less pronounced than was the case with a soap made from  $\frac{1}{2}$  tallow and  $\frac{1}{2}$  cocoanut oil. The hardened oil soap dissolved more slowly in water.†

(2) 80 per cent hardened oil and 20 per cent cocoanut oil saponified in the same way was very hard and white but showed no lathering properties. The odor was slightly rancid.

(3) 30 per cent hardened oil, 25 per cent peanut oil, 30 per cent cocoanut oil and 15 per cent rosin showed a rate of saponification which was normal; the soap was yellowish, the odor and solubility satisfactory, but the lathering properties were not quite as good as normal soap.

The conclusion reached with the hardened oils tested was that very hard soaps could be produced which would show great economy in use, that they gave a poorer lather, that there was some odor over and above that resulting in use of tallow, and that the saponification was slightly slower.‡ Hardened oils were also found to give dark

An example of a satisfactory soap base for toilet soaps is given in the following formula:

15 parts cocoanut oil,  
45 parts tallow oil,  
40 parts Talgol,

and suggestions are made for the manufacture of laundry soaps, white-grained soaps, cold process soaps, transparent glycerine soaps, soap powder, etc. The hardened fat is not suitable for the production of transparent soft soaps or natural grain soaps. (Seifenfabrikant (1912), 1229, 1257.)

\* Seifen. Ztg. (1912), 660.

† Weber (Seifen. Ztg. (1913), 421) gives a somewhat complicated procedure for making soap base with hardened oils of the Talgol type.

‡ Leimdorfer (J. S. C. I., 1914, 206) states that the speed of saponification of hydrogenated fats is greater than the analogous natural fat (tallow) under similar conditions.



fatty acids by the Twitchell process and odor of the fatty acids was not regarded as entirely satisfactory.

A procedure for making milled soap base from hardened oil \* involves the formula:

1200 pounds Talgol extra,  
1200 pounds beef tallow,  
600 pounds Ceylon coconut oil.

The tallow first was placed in the kettle and saponified with 20 degree caustic soda lye somewhat diluted with water. A little salt was added at the beginning of the boiling to prevent lumpiness. The Talgol extra was then added and saponified. This addition gave the stock a different odor which, however, diminished as the operation progressed and the final product possessed the desired odor of good neutral soap. After slow boiling for several hours the stock was allowed to stand over night after it had been ascertained that a sufficient excess of alkali was present. Subsequently the soap was salted out with 24 degree brine, and after settling the spent lye was replaced with 8 degree caustic soda lye. Slow boiling was continued for several hours to complete the saponification and improve the odor. After settling over night the lye was removed and the coconut oil, with the required amount of 30 degree caustic soda lye, was introduced. Less caustic soda was needed than the calculated amount for the coconut oil employed as the saponified stock contained some entrained lye. A small quantity of weak brine was added and boiling continued for several hours. Strong brine was then introduced to salt out the saponified product. After standing 36 hours the stock was withdrawn, solidified in cooling apparatus and subsequently dried. A relatively low temperature was used in drying yet no difficulty was experienced in securing a rapid removal of the moisture. The addition of hydrogenated oil to soft fats prevents adhesion of the resulting soap in the drying apparatus.

The soap base machined perfectly and yielded a first-class finished product. Samples of the soap were stored for several months and then given to unbiased persons for criticism without informing these judges that hydrogenated oil had been used in the make-up of the soap. All united in declaring the product an excellent one and the freshness of the perfume was noted. The lather exhibited by the milled soap was of a good stiff consistency and quite lasting, resembling that afforded by a shaving soap.

On examination, the glycerine-containing lyes derived in the fore-

\* Seifen. Ztg. (1913), 334 and 368.

going method of saponification were found to resemble those obtained when beef tallow was used without additions of the hydrogenated fat.

**Garth \*** states that a grained soap having a desirable hard feel may be obtained by the use of Talgol, as has been proven by practical experience. Also a larger yield is obtained, and since the Talgol products are cheaper than tallow itself, a double advantage is secured. The hydrogenated fat finds application not only in textile and laundry soaps but also in soap base intended for toilet soap manufacture. By itself Talgol is seldom used. In the case of laundry soap 25 to 30 per cent of rosin should be employed. As to shaving and transparent glycerine soaps, see Seifen. Ztg. (1913), 954. Too large an addition of the Talgol to grained soap causes the framed soap to check badly on standing.

**Bergo †** criticizes hardened oil from the point of view of soap making, stating that only a very moderate percentage of the hardened oil in conjunction with other oils and fats can be used, otherwise the lathering quality of the soap is seriously influenced. The somewhat musty odor which soaps containing 30 per cent or more hardened oil show, may be diminished or eliminated through long boiling, or by repeated washing, or by the addition of a suitable perfuming agent; but long boiling, as well as repeated salting out or covering the odor with perfumes, is costly. Another objection, namely, that soaps made with additions of hardened oil lose in lathering quality, is a more important consideration than the odor. The consumer looks upon good solubility and strong lathering properties as essential in soaps. Bergo thinks if success is not attained in removing this objectionable feature, the application of hydrogenated oils in the soap industry will remain very limited.

A further obstacle on a large scale is the color of the product obtained by autoclave saponification. Hardened oil, which as a neutral fat shows a beautiful white color, gives fatty acids which in spite of all possible precautions in the autoclave treatment and even with the use of bleaching material, such as decrolin and the like, appear of a yellow color and in consequence are not suitable for white soaps. If, he states, we do not saponify these oils for fatty acids, but process them as neutral fats and saponify with caustic alkali, then the difference in price as compared with other available fats and oils is so far reduced that it is a question whether the soap manufacturer will use such artificially hardened oils and thereby reduce the quality of the

\* Seifen. Ztg. (1912), 1279.

† Seifen. Ztg. (1912), 1333.

soap. The hopes of the soap maker have been based on the supposition that a fat which would be a substitute in the manufacture of white grain soaps would be found, because the fats and oils now available for making white soaps are very few; while for yellow soaps a whole series of fats are obtainable and these Berge regards as practically no more costly than hardened oil costs to-day. Hence he thinks these new raw materials offer no advantage for the soap industry in Germany on account of their price and defects mentioned.\*

In contrast to the views of Berge, a writer in *Seifen. Ztg.* (1912), 101, refers to the comment that hydrogenated fish oil gives dark unsightly soaps which do not show good lathering properties, and asserts that hardened animal and vegetable oils after careful boiling give soaps which not only are harder than those from the original oil, but are essentially whiter. If dark soaps have been produced, one perhaps can explain the failure on the ground that nickel soaps were present in the hardened oil and through sulfur compounds in the lye were converted into sulfide of nickel. The lack of lathering qualities of soap made from hardened fish or whale oil he contends is a perfectly natural result. Hardened fish oil finds its analogue in tallow. Pure tallow soaps are only indifferently soluble and lather poorly; hence this condition is to be expected in hardened fish oil.

Among a large collection of samples of soaps made from various hardened oils, including many marine animal oils, some were found to have a disagreeable odor like oil which has been distilled. This penetrating odor, which in distillation plants arises through partial decomposition of fatty bodies, is regarded as due to acrolein and is not a necessary consequence of hydrogenation, but is simply a result of over-heating the oil at some time during operation. In carrying out the process technically, too high a temperature should be avoided, thus eliminating the disagreeable odor and producing a hardened oil from which soap of high quality may be prepared. By the addition to hardened fish or vegetable oil of other fatty material, such as palm

\* It should be remembered that in Germany the Leprince and Siveke Patent 141,029 is generally regarded as controlling, and is in strong hands. In consequence the criticism of hardened oil products by professional circles has been perhaps unduly severe, if not in part unwarranted.

Haleco (*Seifen. Ztg.* (1913), 16) feels that the stand taken by Berge is unwarranted, because although the hardening of oils on a large scale has been in practical operation for only a short period, yet in that time there has been a very considerable demand for the hardened material, which demand is daily increasing in the soap industry and other fields. To-day soaps of various qualities, including fine toilet soaps, are being made with a considerable proportion of hardened oil which shows that the new material offers advantages.

kernel or cocoanut oil and rosin, a quick lathering soap may be prepared which satisfies all requirements.

**Hauser**\* is of the view that the application of hardened oils in soap making is for the time considerably limited. It is not impossible that a considerable simplification of the apparatus will enable the soap manufacturers to make use of it more extensively. The more important applications, to Hauser, appear to be in the stearin and edible fat industry. He regards the soaps made from hardened fat as lacking in satisfactory texture and emulsifying properties, as not exhibiting the best of keeping qualities and in storage sometimes even developing an undesirable odor. Then, too, he considers the yield of glycerine to be unfavorably affected by hydrogenation and the fatty acids of hardened oil to be darker than those of the normal oil. In a modern soap establishment it is recommended that cheap, low-grade fat stock be the raw material, which, after purification, is split and the resulting fatty acids are distilled after hardening by treatment with sulfuric acid. In this way with great simplicity and certainty, according to Hauser, fractions of any desired titer may be obtained for various soap compositions without the occurrence of undesirable side reactions which he apparently thinks are unavoidable in hydrogenation processes.†

In the stearin industry the oil may be hardened and then saponified, or the glycerine first may be removed and the fatty acids hardened. It no longer becomes necessary to employ complicated pressing operations to separate stearin from olein as the stearin may be di-

\* Seifen. Ztg. (1913), 141.

† Favorable comment of the Germania Oelwerke products is made by "R. D." (Seifen. Ztg. (1912), 517) who states that these hardened oils have many technical uses. In soap making they are used to advantage and give a good product. Talgol and Talgol extra are used as entire substitutes for tallow. Talgol is best for common household soaps, Talgol extra for toilet soaps. Candelite and Candelite extra on account of high melting point find advantageous application in the stearin and candle industry. He considers the odor of the hardened oils as slight and unobjectionable. The color is gray-yellow. Soaps made from these correspond to the trade requirements. Toilet soaps have a pure white color and do not darken or discolor on standing, and the perfume remains intact. Lower-grade soaps possess a satisfactory appearance, lather well and are sufficiently firm and the odor is satisfactory.

Considering the application of hardened fat in soap making Schuck (Soap Gazette and Perfumer, 1914, 55) states that on account of the high titer of the fat it is not advisable, in fact well nigh impossible, to make a settled soap (without rosin) from the hydrogenated product alone. Such a soap would be too brittle, would crack and would not lather at all.

Train oil (hardened) as a competitor of tallow is considered in Soap Gazette and Perfumer, 1913, 222. See also article by Heller, *ibid.*, 1913, 263.

rectly obtained. The products to which he refers have the following constants:

	Talgol	Talgol extra	Candelito	Candelito extra
Iodine number..	65-70	45-55	15-20	5-10
Melting point. .	35-37° C.	42-45° C.	48-50° C.	50-52
Saponification value. .	192	192	192	192
Unsapoifiable	under 1%	under 1%	under 1%	under 1%
Glycerine content	9-10%	9-10	9-10	9-10

A polemical article by Ribot\* denounces the proposal to use hardened fish or whale oil, no matter how well refined, in the best grade of toilet soaps. Furthermore he does not consider such hardened oils to be substitute fats for tallow or palm kernel oil, but rather that the former may be employed as addition or filling-in fat stock. 20 to 25 per cent may be added to a cheap toilet soap base without detriment; 30 per cent or even 40 per cent may be employed in laundry soaps. In white soft soaps 40 to 50 per cent of Crutolin may be used.† Schaal‡ apparently is in agreement with Ribot that for the highest grade of toilet soap base, tallow should not be materially reduced or displaced by Talgol, but maintains that a soap base may be prepared with 35 to 40 per cent of Talgol which yields a handsome milled soap permanent in quality and suffering no eventual change in color. He also asserts that for ordinary toilet soap base Talgol is in no sense an addition or filling-in fat, but is a real substitute for tallow, and that the same is true of Talgol extra and Candelito respectively for shaving soaps and glycerine transparent soaps; further that the hydrogenation process is an important and fruitful discovery for the soap industry, especially for toilet soap manufacture.

In "Eschweiger" soaps tallow may be completely replaced by Talgol,§ which produces a firmer soap; the yield is good and the odor satisfactory and no objection has been raised to its lathering qualities.

\* Seifen. Ztg. (1913), 142.

† In response to Ribot an article appeared in Seifensieder Zeitung (1913), 173, by Schaal in which the latter makes clear that he did not propose hydrogenated fish or whale oil of the Talgol type for making the very highest grade of soap base; he recommends such fats particularly for toilet soaps of medium quality. Schaal also states that he has never recommended complete substitution of tallow by Talgol fat in the highest grade of toilet soap base and calls attention to the formula which he has published in the past in which a substantial amount of tallow is specified.

‡ Seifen. Ztg. (1913), 173.

§ Seifen. Ztg. (1912), 1230.

Two formulæ are given for filled Eschweger soap according to which a firm marbled product is obtained.\*

Transparent glycerine soaps may be prepared by the use of a hard variety of hardened oil, Candelite being especially suitable, and with this material a soap of very satisfactory transparent appearance and firm consistency may be prepared without using more than a normal amount of alcohol. The following are suitable formulas for the preparation of such soaps:

*Cheap Grade*

90 kilos Candelite.  
90 kilos Ceylon coconut oil.  
84 kilos castor oil.  
144 kilos caustic soda lye, 38° Bé.  
90 kilos sugar dissolved in an equal weight of water.  
100 kilos soap filling.  
30 kilos soda crystals.  
Alcohol q.s.

The soap filling consists of 100 parts salt, 140 parts potash, 40 parts sugar and sufficient water to produce a solution of 21° Bé.

*Better Grade*

90 kilos Candelite.  
120 kilos Ceylon coconut oil.  
90 kilos castor oil.  
166 kilos caustic soda lye, 38° Bé.  
100 kilos sugar dissolved in 75 kilos of water.  
40 kilos soap filling.  
10 kilos glycerine.  
Alcohol q.s.

The Candelite should first be melted, the coconut oil then added and finally the castor oil introduced. Saponification is carried out by the self-heating method, it being desirable to allow the saponified mass to stand an hour or so in order to assure a complete union of the

\* "Eschweger" is a marbled soap, made by saponifying tallow and soft fats together with about one-third of their weight, or more, of coconut oil. The quantity of lye is gauged so as to have the soap very nearly neutral at the end of the operation, as there is no separation of waste lye. All that goes into the kettle also goes into the soap except of course water removed by evaporation. Owing to the properties of coconut oil, such soap, in absorbing a considerable amount of salt solution, becomes of a peculiar consistency, while hot, and crystallization ensues with the formation of "marble" or "mottle" on cooling in the frame. At the same time the soap holds much more water than one which has been mottled by boiling down a soap made entirely of soft fats.

ingredients. Then the sugar solution and filling are added. By proceeding in this manner a clear product is obtained which does not subsequently darken in storage. The amount of alcohol is usually about 3 to 4 per cent, calculated on the soap material. For the better quality a very satisfactory perfuming composition is obtained by mixing equal parts of "palma rosa" oil and artificial geranium oil using 1500 grams to the formula given above. For the cheaper grade of soap a good perfuming agent consists of a mixture of equal parts of Java citronella oil and benzyl acetate. 2000 grams of this mixture should be used for the amount of material specified in the formula first above given.\*

Hardened oil is advantageously used in shaving soaps according to Schaal.† A formula given by him is the following:

50 kilos Talgol extra.  
10 kilos Ceylon coconut oil.  
10 kilos lard.  
20 kilos caustic soda lye, 38° Bé.  
21 kilos caustic potash lye, 37° Bé.

The mixing takes place at a temperature of 52° C. The lyes are first mixed and then added in a thin even stream, stirring well meanwhile in order to quickly get a thorough incorporation. After  $\frac{1}{2}$  to  $\frac{3}{4}$  hour the batch stirs thickly and should be promptly framed. The mass heats strongly in the frames and to take advantage of this the frames should be covered with bagging. By such treatment a section of the soap will show a uniform texture from center to edge.

If it is preferred to prepare this soap by the warm process, it is necessary to add 5 kilos of potash solution of 12° Bé. to the caustic lyes and to prolong the stirring until the mass has the proper body; the kettle is then well covered and its contents given time to react. After 2 to 3 hours spontaneous heating will have set in. The kettle is again opened, the contents well crutched, until uniform, and at the same time perfume can be worked in. The soap is now ready for framing, but the frames need not be covered. The potash solution is added to keep the soap sufficiently fluid to permit of crutching. Without this addition the soap would be so solid and tenacious that the crutch could scarcely operate. The finished soap has a flawless appearance, is almost white, fairly solid and handles well in cutting and packing. .

\* Schaal, Seifen. Ztg. (1912), 955.

† Seifen. Ztg. (1912), 954, and Die Moderne Toiletteseifen-Fabrikation.

A perfume composition which may be employed in this soap consists of the following:

200 grams oil of rosemary.  
200 grains oil of bitter almonds (artificial).  
150 grams oil of lavender.  
75 grams oil of thyme (white).  
100 grams oil of sassafras.  
25 grams oil of wintergreen (artificial).

The odor and lathering properties of soaps made from hydrogenated oil are discussed by Garth\* who considers the characteristic odor of hardened oils of the Talgol type to be in nowise disagreeable. In laundry soaps the aromatic odor of the rosin overcomes the Talgol smell. In making toilet soaps one has to take greater care that the Talgol addition is well gauged as otherwise the proportion of the customary perfuming agents has to be varied. With regard to the diminution of the lathering power he states that soaps from pure Talgol have almost no lather, and in this connection refers to the interesting work of Krafft and other investigators who have shown that the detergent action of soap is dependent upon the nature of the fatty acid, and that there exists an important difference in operation between stearin and olein soaps. Soaps from palmitin or stearin at common temperature are unworkable and develop their detergent or emulsion-forming properties only when a temperature is reached which is approximately that of the melting point of their fatty acids. On the other hand the olein soaps are soluble at ordinary temperatures thus exerting detergent action at low temperatures, but at a temperature of about 80° C. they lose their emulsion-forming qualities. Thus it will be seen why soaps made from pure tallow, or hardened fat, exert a very slight detergent action at ordinary temperature. In working with hardened fat the soap expert should take cognizance of the manner in which the soap is to be used and employ such materials as give the desired detergent property under these conditions.

With 30 to 35 per cent of hydrogenated oil of the Talgol type, Weber† has made a satisfactory soap base holding its perfume well, and although prepared without special manipulation did not, after standing for half a year, show the hardened oil odor when broken. This interval of time is sufficient to determine with certainty whether or not the characteristic odor can be permanently suppressed.

The fatty acids of hydrogenated oil have been examined by Luksck‡

\* Seifen. Ztg. (1912), 1309.

† Seifen. Ztg. (1913), 421.

‡ Seifen. Ztg. (1912), 718 and 742.



with reference to their applicability as candle material. A product having a titer of about 60 was observed to have a greasy feel, to be of amorphous texture and to be lacking in ring and transparency. So far as the samples examined by Lukseh are concerned the product does not appear to be suitable as a candle material without considerable compounding.\*

In saponifying for fatty acids it is not advisable to run above 92 per cent, as otherwise the fatty acids are likely to be dark and the resulting soap off color. When hydrogenated fish oil has been split the fatty acids are saponified in the customary way by carbonated alkali. In finishing, the soap should not be too thin; otherwise, in spite of the high melting point of the hardened fat, the soap will be soft. The soap should be separated only with an excess of lye. It separates rather badly and should be allowed to stand two or three days in the kettle in order to harden. A soap made from Talgol with 30 per cent of rosin is of fair appearance, lacking, however, the transparency of soap prepared with a large content of palm kernel oil. While the color is good, there is a noticeable dullness of surface. After drying and pressing it acquires a satisfactory glossy finish. While a soap made only from hardened fish or whale oil has practically no lathering properties, the addition of 30 per cent of rosin greatly improves this defect and very good lathering properties result.†

\* Even if it were possible, "J. G." states (Seifen. Ztg. (1912), 1146), to split the fat completely on a commercial scale, the color of the fatty acids excludes the direct application of the product in candle manufacture. He even claims that it is necessary to subject the saponified product either to distillation or to pressing, and that in the latter case the poor crystallization of the fatty acids gives rise to difficulties. But he adds that the ordinary stearin candle is made up largely of a mixture of palmitic and stearic acid in which a certain ratio between the two fatty acids must exist to maintain the quality of the candle. Hence in judging hardened fat with reference to its application as a candle material, the composition of the original fat is not unimportant, for useful mixtures may well be obtained through careful selection of the raw materials. In those cases where the nature of the chemical individuals derived by hydrogenation have not been entirely made clear, as in the case of fish and whale oil, further practical investigations will be necessary to show whether or not hydrogenation will afford a generally useful product in candle manufacture.

† Seifen. Ztg. (1912), 870.

A few years hence when oil hydrogenation has found its measure and the more important points concerning it have reached definite settlement, the allotment of space to a number of the discussions appearing in this chapter hardly would be warranted, but at the present time when many are desirous of having at hand a review which comprises all or nearly all the published work to date, containing though it does a considerable divergency of opinion, there appears ample justification for the inclusion of such discussions as those given above.

A tallow-like product which has been brought into the market as "Talgit" is prepared by hydrogenating fish or whale oil. Müller has examined this product \* and has reported the acid number as 12.8 and the iodine number as 49. The fatty acids exhibited a titer of 39.4° C. When Müller attempted to saponify the fat by the Twitchell process, dark colored fatty acids were produced, caused, it is supposed, by oxidation during saponification. Müller observes that copper, iron and lead tend to cause a discoloration of fat which is treated by the Twitchell process, and he concludes that the traces of nickel which were present in Talgit acted in a similar manner. When he subjected the fat to cleavage by the autoclave process very light colored fatty acids were obtained. A pressure of 10 to 11 atmospheres was maintained in the autoclave for a period of 8 hours and the resulting fatty acids were found to contain about 2.5 per cent of unsaponified fat. The following results were obtained from an examination of the fatty acids:

Acid number of the fatty acids .....	194.0
Saponification value of the fatty acids. . . . .	198.0
Titer . . . . .	39.2° C.
Acid number of the liquid fatty acids.....	186.3
Saponification values of the liquid fatty acids. . . . .	191.2
Iodine number of the liquid fatty acids. . . . .	100.0
Titer of the liquid fatty acids.....	14.3° C.
Titer of the solid fatty acids. . . . .	48.7° C.

The fatty products of the saponification pressed very readily and about 35 per cent of solid fatty acids were obtained whose low titer (48.7° C.) indicates, according to Müller, that fatty acids in addition to or other than stearic and palmitic acids are present, for the solidifying point of mixtures of palmitic and stearic acids is above 53.5° C. The presence of iso-oleic acid which causes a lowering of the titer of stearic acid obtained by distillation is not to be expected in this case, but Müller has not further investigated the acid mixture to identify any of its components. As the fatty acids pressed satisfactorily, Müller concludes that the stearic acid was technically pure, hence the low titer cannot be ascribed to the presence of undue amounts of liquid fatty acids. The expressed fatty acids, or oleic acid, obtained as stated above, exhibited a straw yellow color and showed the characteristic odor of hardened fish or whale oil. Müller states that for many purposes the iodine number of these liquid fatty acids is too high. He concludes that so far as this product is concerned the hydrogenation of the unsaturated fatty acids does not proceed successively

\* Seifen. Ztg. (1913), 1376.

so as to convert all of the unsaturated bodies having two or more double bonds into bodies having only one double bond before the latter bodies are hydrogenated, or in other words that linoleic and linolenic acids are not all converted into oleic acid before stearic acid forms, but instead of this that reduction takes place throughout, so that all types of unsaturated compounds are more or less reduced simultaneously. This observation is of interest because, as Müller notes, the presence of highly-unsaturated bodies of the nature of drying oils in such products is often undesirable.

Müller prepared soap from Talgit and found it to have little or no detergent and lathering properties which he notes is to be expected with fats of this titer, and in consequence of these properties, products of the nature of Talgit cannot be used as the essential fat material, but should be used only as additions to the main fat stock.

Commenting on the observation of Müller regarding the properties of Talgit, Dubovitz (Seifen. Ztg. (1913), 1445) notes that the investigation of the fatty acids of hardened fish oil indicates that there is present an acid whose molecular weight is less than that of palmitic acid. Also it is stated that it is possible to obtain stearic acid or stearin having a titer of 53 to 55 degrees from strongly hardened fish oil simply by pressing.

Müller (Seifen. Ztg. (1914), 8) discusses the comments of Dubovitz and points out that mixtures of two saturated fatty acids crystallize well from the stearin manufacturer's point of view, while mixtures of three or more fatty acids as a rule produce an amorphous mass.

The contention of Dubovitz that the low titer of stearin can be explained by the presence of saturated fatty acids with less than 16 carbon atoms in the molecule and derived from the corresponding unsaturated compounds by hydrogenation rests on the assumption of the existence of just such unsaturated fatty acids, or their glycerides, in fish oils. Proof of this is said to be lacking up to the present. Even the presence of hypogeic and physetoleic acids in these oils is still doubted. It is held that the low titer of the stearin in question was due to the presence of unsaturated fatty acids. (Seifen. Ztg. (1914), 33.)

In discussing the distillation of fatty acids, Hajek\* states that some difficulties are encountered when working up hydrogenated oils to produce fatty acids. He states that all fats which are treated when hot with air or other gases for a considerable length of time, after autoclave saponification, yield dark colored fatty acids and that this discoloration is due to a chemical change which takes place in coloring agents present, similar in character to that which occurs in the distillation of fatty acids at elevated temperatures, or with an insufficient proportion of superheated steam.†

\* Seifen. Ztg. (1913), 445.

† The idea which has been entertained that hardened triglycerides could be directly used for candle material is out of question, as no one would care to inhale the vapors

Normann has made candles with stock obtained from hardened fish or whale oil which burned brightly and without odor, similar to the best grade of stearin candles.\*

The properties of hardened castor oil have been noted by Garth.† As is generally known, castor oil differs in many respects from other common oils in such respects as its high viscosity, solubility in alcohol and difficulty of salting out its soaps by electrolytes. The constants of one sample examined by Garth are as follows:

Acid number . . . . .	3.5
Saponification number . . . . .	183.5
Iodine number . . . . .	4.8
Acetyl number . . . . .	153.5
Acetyl number of the fatty acids . . . . .	143.1
Acid number of the fatty acids . . . . .	184.5
Saponification number of the fatty acids . . . . .	187.9
Melting point of the fat . . . . .	68° C.
Melting point of the fatty acids . . . . .	70° C.
Melting point of the acetylated acids . . . . .	47° C.

These results indicate that the saponification and acetyl number do not change. The difference between the acid number of the fatty acids and their saponification number points to the formation of lactones.

From the point of view of soap technics, it may be noted that the hardened product saponifies with dilute lye about as easily as common

coming from candles in which acrolein was being generated. Any large proportion of nickel in the fat would also interfere with the burning qualities. (Sach, *Zeitsch. f. angew. Chem.*, 1913, No. 94, 784.)

The slight lathering properties of soap made from hardened tran is to be expected, because this fat finds its analogue in tallow. Pure tallow soaps are very difficultly-soluble and lather very poorly so the same property may be looked for in hardened fish oil or whale oil. (Seifen. Ztg. (1912), 1003.)

The dark colored soaps which have been noted by some users of hardened oil may be due to traces of nickel soap in the oil which react with sulfur compounds in the lye, resulting in the formation of nickel sulfide and consequent discoloration. (Seifen. Ztg. (1912), 1003.)

The odor of hardened tran is very much like that of distilled oils and recalls the penetrating disagreeable odor which is observed in distillation works and which is apparently due to the partial decomposition of fatty acids with the production of acrolein bodies. Odors of this character materially affect the quality of the soap, but this trouble may be avoided if greater care is taken in the hardening process to avoid over-heating of the oil or fat. By skillful working at not too high a temperature, the disagreeable odor does not appear and the tran is rendered completely odorless. From this product a soap may be made which is beyond criticism.

\* Seifen. Ztg. (1914), 263.

† Seifen. Ztg. (1912), 1309.

castor oil. Further, soap prepared from the hardened product, in spite of its high melting point, like castor oil soap, has a similar lack of sensitiveness against salt solutions and behaves in this respect like the fats of the cocoanut oil group. Like the fats of the latter group, the hardened fat may be saponified at a temperature of about 80° to 90° C. While a soap with 30 per cent fat content made from ordinary castor oil is liquid, the corresponding soap from hardened castor oil is very firm, but the latter soap does not possess the property of lathering in the least.

With regard to tariff rating on hardened oil **Böhm** \* thinks beyond question the hydrogenated product should not be declared and rated like the untreated oil and draws an analogy between raw oils and their hydrogenated products and formaldehyde or acetaldehyde which yield chemically different bodies, respectively methyl and ethyl alcohol, by taking up hydrogen.

It is contended † that Böhm's illustrative use of formaldehyde, which body through the addition of two atoms of hydrogen is transformed into methyl alcohol and thus into an essentially different body from the tariff point of view, is not entirely analogous with respect to hardened oils, for oils are not unitary chemical individuals, but are mixtures of triglycerides of various fatty acids. Also it is held that hydrogenated oils are not essentially single chemical individuals, like tristearin, but are mixtures of various fatty acid triglycerides in which mixtures, of course, tristearin is present in much greater quantities than in the original oil. A differentiation for tariff purposes on the ground of chemical composition is thus practically impossible.‡

Dr. Bela Lach, in the *Seifen. Ztg.* (1912), 1245, discusses American soap manufacture and refers to the Fels Naptha Soap Works of Philadelphia, as being users of hydrogenated oil. He says that Fels Naptha soap contains from 10 to 15 per cent of benzene of high boiling point, and that the raw materials are in a large part cotton and corn oil. Only a relatively small proportion of hard stock, such as tallow or

\* *Seifen. Ztg.* (1912), 738.

† *Seifen. Ztg.* (1912), 1003.

‡ An article by Harmsen (*Seifen. Ztg.* (1913), 638-39 and 661-62) discusses the matter of tariff adjustment of hardened fats, and he states that by the hardening operation the consistency and other qualities of the oil are so modified that a recognition of its origin is in most cases impossible either by taste, smell or chemical test. Chemical analysis can determine only whether the fat is of animal or vegetable origin. The Hamburg authorities have arrived at the conclusion that hardened fat or oil must be taxed according to the properties and quality acquired by hardening. Harmsen also discusses the position of Talgol from the tariff standpoint in *Seifensieder Zeitung* (1913), 745.

palm kernel oil, is used. The amount of this material employed is, however, reduced because this concern has been able to make use of hydrogenated oil, a material which they have thoroughly tested. At this plant Lach states he saw samples of hardened cotton and corn oil, as well as various kinds of hardened fish oil which were of a remarkably fine character. They had the hardness and appearance of fine tallow, were beyond criticism as to odor and could be worked up into a soap in a satisfactory manner.

A hardened oil of relatively low titer, bearing the trade name of "Krutolin" (or Crutolin),\* is discussed in the *Seifensieder Zeitung* (1913), 930 and 954, and as some of the observations may be of use in the handling of other more or less similar hydrogenated products the following data is here included.

On account of the great demand for good fats and oils in edible-fat manufacture, the prices of these have increased very materially, and it has become continually more difficult to obtain fats which remain white on boiling. Therefore hardened oils such as Krutolin, which may be obtained of uniformly good quality, promise to be of decided utility. It is said that Krutolin has the advantage of being cheaper than lard and cottonseed oil, and that in addition it is, as has been proven by long-continued experiments, a good substitute for lard and white cottonseed oil. When used for barrel soaps, Krutolin, alone, has a tendency to form sirupy, stringy soaps. Therefore, it is desirable to supplement it by the proper addition of other fats. In practice it has been shown that the danger of "lengthening" of unfilled white soft soaps is greater than when more or less potato flour is used as a filler. Hence it is recommended that the percentage of Krutolin employed be kept somewhat lower for such unfilled products.

As mutton tallow, cottonseed oil, peanut oil and lard, or their fatty acids, in Germany are the usual or principal raw materials for white soft soap, it is stated that under present market conditions a considerable saving is attained in the manufacture of soaps if these fats are replaced, even only in part, by Krutolin. In combination with the above-named raw materials Krutolin furnishes a very white soap for both unfilled or filled goods. It is self-evident that a primary condition for the production of a totally white soap is cleanliness of working. Furthermore, it is necessary to pay attention to the alkali and especially the potato flour as these are often of varying origin, and are not always suitable. Many 50-degree caustic potash lyes give perfectly water-white solutions when diluted; others, however, show a yellow tone. With filled soaps the quality of the potato flour has a strong influence on the character of the finished product. Every shipment should be tested for color and to ascertain whether the flour has been treated with acid. Potato flours containing acid are to be excluded for filling white soft soaps, as they produce an after-darkening. The kind of water used also has some influence on the color of these soaps.

A stock for unfilled figged soap containing Krutolin follows:

1500 kg. mutton tallow
900 kg. cottonseed oil
600 kg. Krutolin
<hr/> 3000 kg.

On account of the high titer which mutton tallow possesses and in recognition of the fact that Krutolin easily favors the "lengthening" of the soap, one must

\* Krutolin is stated to be a substitute for "technical" lard and American cotton oil (*Seifen. Ztg.* (1913), 1386).

from the beginning count on a strong increase of carbonated alkali to reduce the causticity of the caustic potash lye. It is possible, in the above stock, to use 30 kg. 96 to 98 per cent potash to 100 kg. of 50-degree caustic potash lye. It will often be advisable, especially during the warm season, to substitute ammonia soda solution for a part of the potash solution, in order to secure an easy and rapid figging of the soap.

After completion of the boiling, samples are to be carefully tested to ascertain if the soap has been sufficiently shortened by carbonated alkali. Samples placed on glass must remain liquid a long time, and on stirring after cooling must not show any stringiness. Should the soap still remain tough and gum-like a later addition of concentrated potash or soda solution is necessary in order to produce a satisfactory product. On account of the large amount of carbonated alkali which can be absorbed, the yield of this soap is very good.

The mutton tallow can be omitted and a somewhat larger amount of white lard substituted. The composition would then be about as follows:

1600 kg. lard
750 kg. cottonseed oil
650 kg. Krutolin
<hr/> 3000 kg.

As lard has a considerably lower titer than mutton tallow, the amount of shortening material used with this stock must be decreased accordingly. With the stock first given, which contained a large amount of mutton tallow, additions of caustic soda lye were not necessary, but in this case, where softer fats form the basis, it is advisable to add about 20 per cent of caustic soda lye in the boiling. The neutral fats in this stock can be replaced by fatty acids, but as soaps from neutral fats are whiter, this is not to be recommended. A moderate filling with flour is advantageous when using fatty acid stock. A figged soap with a little filling can hardly be distinguished by visual examination from one which is unfilled. For the above stock of 3000 kg. the following filler is recommended:

300 kg. best potato flour.
600 kg. 12-degree potash solution.
300 kg. lye, 30° Bé.

The filler is to be added in the morning if the soap has cooled sufficiently over night. The soap is perfumed with sal-ammoniac, turpentine, safrol, oil of camphor, lemon oil or suitable mixtures of these.

For a first-class "sal-ammoniac-turpentine" soft soap, where particular value is laid upon the resulting white color, and less on the figged effect, mutton tallow and cottonseed oil may be left out and Candelite and Talgol substituted in part therefor. The composition would then be the following:

2000 kg. Krutolin.
1000 kg. Candelite.

For the reduction of the causticity 30 kg. potash should be used to every 100 kg. 50-degree caustic potash lye. On boiling about one-third caustic soda is to be added. To the latter 25 kg. ammonia soda are added to every 100 kg. soda. These alkalies are dissolved separately, mixed and the lye diluted to the required strength.

The above stock gives a soap of special toughness. Therefore, it may be necessary to add more or less soda or potash solution according to the result of tests made from time to time, until the soap possesses the desired normal characteristics. "Sal-ammoniac turpentine soap" made according to this formula possesses a very white

color and by use of first-class potato flour can be filled up to 25 per cent without influencing the color.

The filler is made up as previously mentioned, but must have an addition of potash filler. Its make-up thus becomes:

750 kg. potato flour.  
1500 kg. 12-degree potash solution.  
375 kg. potash filler.  
750 kg. 30-degree "take-off" lye.

In order to more surely prevent the lengthening of the soap ammonia-soda solution also may be used in part in the filler instead of potash solution. For second and third quality soap which can be filled in a similar manner with 50 and 75 per cent of potato flour, the formula and boiling remain the same. These filled "sal-ammoniac turpentine" soaps should be perfumed rather strongly with sal-ammoniac and some turpentine, for prospective purchasers judge the soap not only by its white color, but also by the more or less strong ammoniacal odor.

As already mentioned, the yield of such soaps is said to be increased by the use of Krutolin. This is explained by the increased ability to take shorteners. For example, a "sal-ammoniac turpentine" soap filled with 50 per cent potato flour, gave a yield of about 250 per cent.

Krutolin is not available for natural grain and green soft soaps, as here its qualities do not make it a substitute for either tallow or linseed oil. Tallow is necessary for natural grain soaps; at least up to now it has been impossible to produce a faultless grain formation with Krutolin or Talgol. Krutolin is also not suited for a perfectly clear transparent soft soap.

From long continued tests in a large way it has been shown that Krutolin can also be added to the stock used in making bar soaps, insuring light color with good pressing qualities.

A stock giving a light yellow soap which presses well, is the following:

1200 kg. Krutolin  
1200 kg. fatty acids of Talgol  
300 kg. fatty acids of by-product coconut oil  
300 kg. fatty acids of palm kernel oil  
3000 kg.  
450 kg. rosin = 15 per cent  
3450 kg.

Under normal treatment and good cooling the above stock will furnish a soap of adequate firmness. Of course, the amount of rosin added has an important influence on the solidity of the soap. With large amounts of rosin the use of soft fats must be minimized, as otherwise there is danger of obtaining too soft a soap in spite of the cooling treatment.

A stock with 20 per cent rosin has the following composition:

800 kg. Krutolin  
600 kg. fatty acids of light bone fat  
1000 kg. fatty acids of Talgol  
300 kg. fatty acids of by-product coconut oil  
300 kg. fatty acids of palm kernel oil  
3000 kg.  
600 kg. rosin = 20 per cent  
3600 kg.



To obtain sufficiently solid soaps it is important to separate sharply on salting out so as to secure a good grain. By doing this the appearance of cake soap may be somewhat marred. This, it is further stated, is not to be feared so much with cooled soaps, as undesirable segregation cannot occur to any material extent during the rapid solidification. This is one of the main advantages of cooling machines in addition to the rapid production of goods ready for shipment. If only by-product cocoanut or palm kernel oil from edible fat manufacture are to be used for the stock instead of the best palm kernel fatty acid, it will be necessary to reduce the proportion of rosin as the resulting soap may otherwise be too soft. These by-product cocoanut or palm nut oils almost always contain sesame or other similar oils, and influence the soap produced from them. When Krutolin is used in this manner it is advisable to perfume with safrol, lemon oil, etc., before cooling in order to cover the peculiar odor of this raw material which is disagreeable to some people.

For settled yellow rosin grain soaps Krutolin can also be used to advantage as it improves the base for later coloring. The action of crude palm oil used for coloring will be materially stronger with a clear soap base, than if, for instance, dark bone fat has produced a base difficult to cover.

The composition of the stock is the following:

600 kg. by-product cocoanut oil
900 kg. Krutolin
600 kg. fatty acids of light bone fat
450 kg. fatty acids of Talgol
450 kg. crude palm oil
3000 kg.
600 kg. rosin = 20 per cent
3600 kg.

Here also the condition of the finished soap must be the regulator for its composition. For instance, if the soap is too soft, the percentage of rosin or Krutolin is to be reduced.

Krutolin also finds a use in making white wax grain soaps and various grades of textile soaps. Where the kind and color of the soaps allow, as has been repeatedly found with textile soaps, Krutolin should be split, in order not to lose the glycerine.

Krutolin can be used to advantage as an addition fat in making soaps by the cold process, although care should be taken in its use. With unfilled toilet soaps about 30 per cent Krutolin may be used with about 70 per cent of cocoanut oil. If the soap is to be filled, the percentage of Krutolin should be correspondingly reduced, since otherwise the soap would suffer in appearance and would be poorly bonded.\*

In preparing a white soft soap Bergo (Seifen. Ztg. (1913), 1220) uses 1000 kg. fatty acids of cotton oil to 200 kg. of Candelite. 900 kg. of 30° Bé. caustic potash lye and 300 kg. of 25° Bé. caustic soda lye are used together with 100 kg. of carbonate of soda lye of 30° Bé. The caustic potash lye is reduced with carbonate of

\* Seifen. Ztg. (1914), 8.

potash solution. The lyes are put in the kettle first, the fatty acids slowly added and then the Candelite.\* (Chem. Abs. (1914), 588.)

Hydrogenated linseed oil has been put on the market under the name of "Linolith" by the Germania Ölwerke.† Two grades are manufactured. One grade has a melting point of 45° C., and the other melts at 55° C. Both grades show a saponification number of 188 to 195 and a glycerine content of 9 to 10 per cent. Linolith has not been used extensively in white soaps as it is off color, but is serviceable for the preparation of rosin or "Eschweger" soaps and the like. While the raw material, linseed oil, is liable to cause yellowing or after-darkening of soaps or the sweating out of drops of a yellow liquid, the hardened oil is thought to be free from these objections, but caution is advised in its use until thorough tests have been carried out.‡

Soaps made with hardened linseed oil (Linolith) and rosin are of good quality and the odor and color are excellent.§ The following formulæ have been tested:

\* The character of soaps made from hardened oil in conjunction with cottonseed or peanut oil is discussed in *Der Seifenfabrikant* (1913), 31.

† Talgol, Candelite, Krutolin and Linolith have taken a place in the German market and are listed among the fats regularly quoted. (See *Seifen. Ztg.* (1913), 1386.)

‡ In Germany the price of fish and whale oils fluctuates to some extent with that of linseed oil by reason of the demand for these oils by oil-hardening concerns. (*Seifen. Ztg.* (1913), 1385.)

Linseed oil is in increased demand for the manufacture of hardened oils and edible compounds. It is stated that in North America this oil promises to become an important raw material for the hydrogenation industry. (*Seifen. Ztg.* (1913), 1277.)

R. H. Adams, president of the American Linseed Company, attributes considerable importance to the hardening process as applied to linseed oil. "The hydrogenation process," Adams states, "is merely in its infancy and is bound to exert a powerful influence upon the oil markets, and will prevent the price of linseed oil from ever going to the low levels which have been reached in certain years of the past." He states that the process would not affect linseed oil alone, but as the process was applicable to other vegetable oils and to fish oils, the question of comparative prices would largely determine the extent of consumption in the case of each oil. The increased outlet for linseed oil afforded by virtue of the hydrogenation process was generally credited to the soap trade. While consumption of oil for soap-making purposes undoubtedly has increased, Adams states that another outlet, and one which may assume very large proportions, is found in the edible trades, and even now large quantities of linseed oil are being thus consumed on the Continent. (O. P. & D. R., March 10, 1914.)

‡ *Seifen. Ztg.* (1913), 1299.

§ *Seifen. Ztg.* (1914), 231.

	A	B	C	D
Linolith, M. P. 45° C., or its fatty acids..	1600 lbs.	1600 lbs.	.....	.....
Linolith extra, M. P. 55° C., or its fatty acids.....	.....	.....	1500 lbs.	1500 lbs.
Fatty acids of palm kernel oil.....	400	200	400	300
Fatty acids of cocoanut oil.....	.....	200	.....	.....
Fatty acids of peanut oil.....	.....	300	500	500
Fatty acids of Talgol.....	500	.....	300	.....
Soft fat.....	500	700	300	700
Rosin.....	750	1050	900	1200

The fatty acids were saponified with carbonate and the neutral fat with 30 degree caustic soda. The Linolith extra was found capable of carrying a higher proportion of rosin than the regular Linolith.

Linolith does not exhibit any marked odor such as is observed in the case of much of the hardened fish oil on the market and is regarded as suitable for the manufacture of white grained soaps.\* The following procedure has been tried and a satisfactory product obtained. 50 parts of Linolith, 10 parts of a tallowy fat and 40 parts of fatty acids derived from a vegetable oil were employed. The Linolith and tallowy fat were saponified and it was noted that saponification progressed rapidly. The product was bleached with Blankit and salted out. After settling it was combined with stock derived from the separate saponification of the vegetable oil, and well boiled and salted out. The soap was duly grained and afforded a product of excellent feel and good odor. The color was not a pure white.

The difficulties in using hydrogenated linseed oil (Linolith) in white-grained soaps, according to Wilhelmus,† have been that the color was not sufficiently light and the lathering properties were deficient. The texture of the soap was unsatisfactory and cracks occurred on standing. In investigations directed toward the elimination of these objectionable features Wilhelmus found that much depended on the manner of cleavage of the hardened linseed oil. While with autoclave treatment saponification to the extent of 88 to 90 per cent gave fatty acids of good color, it was not found feasible with the Twitchell reagent to exceed 80 to 82 per cent, as the resulting fatty acids otherwise were too dark for white soaps. Pfeilring reagent afforded better results and Wilhelmus regards this cleavage compound to be of specific value in splitting hardened oils. Benefit is derived by adding to hydrogenated linseed oil a quantity of an oil, such as peanut oil, which splits easily, yielding light colored fatty acids. By subjecting the hardened oil to cleavage under these conditions a better grade of fatty acid may be obtained.

\* Seifen. Ztg. (1914), 140 and 167.

† Seifen. Ztg. (1914), 257.

In making the soap about 40 per cent of hydrogenated linseed oil (Linolith) may be employed. After saponification with alkali and graining in the kettle, the product is bleached. For this purpose a bleach consisting of 91 parts of water, 5.8 parts of sodium bisulfite, 2 parts of sulfuric acid and 1.35 parts of zinc dust are used for 1000 parts by weight of the fat. The use of soap-cooling apparatus, in place of frames, enables a better control of the color. The addition of 10 to 15 per cent of castor oil improves the solubility and lathering qualities of the soap. 15 per cent of castor oil is the maximum.\* If still higher lathering properties are required "Saponin" powder may be added.

\* The preparation of soaps with fatty mixtures consisting of saturated fats, such as those derived by hydrogenation, with unsaturated fats or oils has been made the basis of an application for German Patent by Worms and the novelty of the idea is criticized in *Seifensieder Zeitung*, 1914, 392.

## CHAPTER XVI

### USES OF HYDROGENATED OILS AND PROPERTIES OF CERTAIN HARDENED PRODUCTS

Ittner\* states that the hydrogenation process has been worked out by a number of soapmakers, that hydrogenated oils have been and are used on a comparatively large scale in soapmaking but that their principal employment up to the present time has been in the manufacture of edible fats.

The hydrogenation process has reinstated whale oil as an important fatty commodity. The Oil, Paint and Drug Reporter† alludes to the status of this oil as follows:

"About fifty years ago whale oil found an extensive sale for illuminating and lubricating purposes. So established became its use as a burning oil, stories are told that concern was sometimes expressed as to the means of future lighting when the supply of whale oil should be exhausted. Stocks of the oil were in the early days occasionally insufficient for the demand and there was apparently some color to these fears. With the advance of the petroleum industry and the assurance of relatively low cost of burning and lubricating oils, the whaling industry was confronted with a power that was destined to undermine its staunchest support, and gradually it had to yield to the overwhelming economic force until about five years ago when another shift in the fortunes of trade opened new and unexpected opportunities for whale oil. The restoration came through the successful development of the hydrogenation of oils, which has enlisted foreign interests in the whaling industry on a large scale, and the production has reached under modern methods limits that can put to blush the records of early years. According to the latest statistics, the world's annual output of whale oil amounts to more than 800,000 casks. Instead of illuminating our darkness, it now serves mankind liberally as a soap material, for which field it is well adapted, while some measure of success has been attained through the hydrogenation process for edible requirements.‡ In place of the old whaling schooners modern vessels are now employed and present refining methods are much more scientific and capable."

The reduction of clupanodonic acid by means of hydrogen and colloidal palladium yields stearic acid and a mixture of saturated acids of low melting-point. From this and other observations the view is advanced that clupano-

\* J. Ind. Eng. Chem., 1915, 936.

† Jan. 25, 1915, 9.

‡ In view of the stringency in Germany of consistent fats, brought about by the war, the use of hydrogenated fish oil or other hardened oil is advanced as fitting. Chem. Ztg., 1914, 1131 and Seifen Ztg., 1915, 1011 and 1132.

donic acid contains a mixture of isometric tetra olefine carboxylic acids, in part having branching hydrocarbon chains.\*

The results of hydrogenating torpedo liver oil are reported by White.† The oil was hydrogenated at a temperature at 200° C., in the presence of reduced nickel supported on asbestos. Hydrogen was simply bubbled through the oil which was placed in a vessel heated by an oil bath. An oil of pleasant nutty odor was prepared by hydrogenating for a few hours.

According to Tsujimoto‡ oils from the livers of different species of Japanese sharks contain a large proportion of unsaturated hydrocarbons, up to 90 per cent in the case of *Squalus Mitsukuri*. The chief constituent is a hydrocarbon,  $C_{30}H_{50}$ , which is a colorless oil, with sp. gr. 0.8587 at 15° C. It has pronounced drying properties and forms a bromine addition compound,  $C_{30}H_{50}Br_{12}$ , and a hydrogen addition compound,  $C_{30}H_{62}$ . The name "squalene" is suggested for this hydrocarbon.

**Hydrogenation Procedure.**—3.3115 g. of the hydrocarbons of shark-liver oil § were dissolved in 30 cc. of ether in a shaking bottle. To this solution 0.5 g. of Loew's platinum black was added. The bottle was then connected to a gas burette, which, in turn, was connected with a hydrogen holder. Hydrogen was prepared from pure zinc (Merek) and dilute sulphuric acid, and before entering into the burette, it was washed and dried by bottles containing a solution of potassium permanganate and concentrated sulphuric acid. By vigorously shaking the bottle, hydrogen was conducted into it under the mercury pressure. After two hours forty minutes, the absorption ended; the volume of hydrogen absorbed, together with a little leakage, was 1120 cc. The hydrogenated compound, left on evaporating off ether, was found to be a colorless oil, resembling in its appearance the so-called liquid paraffin. It has the following properties: Sp. gr. at 14° C., 0.8125; b.p. (10 mm. pressure) 274° C.; solidifying pt.; at -20° C. it remained clear and mobile; 80° -C., solidified to a transparent jelly which at -35° C. regained its mobility; ref. index at 20° C., 1.4525. It was not readily acted on by concentrated sulphuric acid, even at 100° C.

**Elementary Analysis.**—(1) 0.1610 substance gave 0.5022  $CO_2$ , 0.2114  $H_2O$ .

(2) 0.1910 substance gave 0.5959  $CO_2$ , 0.2523  $H_2O$ .

C=85.07, 85.09 per cent; H=14.69 per cent, 14.78 per cent.

$C_{30}H_{52}$  requires C=85.21 per cent, H=14.79 per cent.

Molecular weight determination, by freezing-point method, 0.2982 substance in 11.1030 benzol,  $d=0.31^\circ C$ . Mol. wt.=433.

$C_{30}H_{52}$  requires mol. wt.=422.5.

The substance has, therefore, been confirmed to be a compound of the empirical formula  $C_{30}H_{52}$ . As  $C_{30}H_{52}$  is of a type of the general formula  $C_nH_{2n}+2$ , it appears that the hydrocarbon  $C_{30}H_{50}$  belongs to the aliphatic compounds.

\* Seifen. Ztg., 1914, 1072; Riedels Berichte. 1914.

† Transactions American Fisheries Society, December 1914, 88.

‡ J. Chem. Ind. Tokyo, 1916, 19, 277; J. S. C. I., 1916, 609.

§ Tsujimoto, J. Ind. Eng. Chem., 1916, 889.

As to the uses of the hydrocarbon, Tsujimoto states that only a brief investigation has been made as yet. It may be mentioned, however, that for technical purposes, the hydrocarbon may be used for paints, varnishes, lithographic inks, and oil colors. The hydrogenated product, which, in its appearance, is very similar to so-called liquid paraffins and, at the same time, far more stable for cold, will be a useful material for lubrication of machines.

The medicinal use of the hydrocarbon, possible for the same purpose as cod-liver oil, will perhaps be most interesting, but careful researches are necessary to settle this question.\*

Calamary oil † is obtained from the internal organs, especially the livers, of various species of cuttle-fish. The oil, especially the refined, is easily hydrogenated by nickel catalyzer, giving, according to Tsujimoto, a white tallow-like fat of M.P. 43 to 44° C. and iodine value of 49.25. Tsujimoto believes the chief use of the oil will probably be as a raw material for hardened oils, as its price is below that of other fish oils.

Some details of the work of Tsujimoto on elupanodonic acid are of interest in view of the present extensive application of the hydrogenation process for the deodorization of fish and whale oils (see page 360). Tsujimoto ‡ has observed a rough relationship between the amount of odor of an oil and the degree of unsaturation. The author attributes the disagreeable odor of marine animal oils largely to the presence of glycerides of highly-unsaturated fatty acids, especially those of the series  $C_{2n}H_{2n-4}O_2$ . Thus, Japanese sardine oil, which contains a large proportion of elupanodonic acid, has a much more pronounced fishy odor than herring, whale, dab, or turtle oils, which contain less of that acid. This was supported by the fact that on treating a solution of the fatty acids from Japanese sardine oil with bromine, filtering off the insoluble octobromide, and reducing the brominated fatty acids in the filtrate. The acids obtained were practically free from the original unpleasant odor, though still possessing an odor. The precipitated octobromide was odorless, but when reduced with alcoholic hydrochloric acid and zinc dust, it yielded elupanodonic acid with the characteristic fishy odor of the oil. Tsujimoto, therefore suggests that future investigations of the problem of deodorization of these oils should aim at either the complete removal of glycerides of the elupanodonic acid series or of their conversion into non-odorous compounds.

As yet no satisfactory method of extraction of the elupanodonic acid has been found, but the hydrogenation process has accomplished the alternative which Tsujimoto advanced.

In a discussion of the fish-oil industry in Hokkaido (Japan), Ueno § observes that the body oils of herring, sardine, flat fish, sculpin, etc., which are obtained in that locality, are of inferior quality and are used in the hardened oil industry.

\* See also Chem. Abs., 1918, 1004.

† Tsujimoto, J. Ind. Eng. Chem., 1916, 801.

‡ J. Coll. Eng., Imp. Univ., Tokyo, 1908, 4, 181-191; J. S. C. I., 1909, 318.

§ J. Chem. Ind. Japan, 1915, 798; Chem. Abs., 1916, 535.

Evidently, in the soap industry, hydrogenation has created very little sensation in this country, Schuck states,\* and he doubts if the majority of soap manufacturers have shown an absorbing interest in this question as they have not been forced to accept hydrogenation as a fact to be reckoned with in the manner the soap manufacturers on the other side of the ocean have had to do.

Two years ago when hydrogenated fats were put on the European market in large quantities they were received with a good deal of skepticism, no doubt due to the novelty of the thing, and then the price was not attractive enough in comparison to the disposable raw materials. Since then, palm-kernel oil, Ceylon coconut oil, white greases, etc., have gone up in price to such an extent that the soap manufacturer was only too willing to try his luck with hydrogenated fats. It is indeed, an accomplishment, Schuck states, to produce a very satisfactory base soap for toilet soaps from hardened whale oil when we consider that only a few years ago such an oil would have been totally unsuitable for either toilet or laundry soaps. It is quite evident that a white soap, for instance, made from hardened whale oil alone would be just as unsuitable for the trade as one made from a high-titre tallow. The soap would hardly lather, would be too brittle and would crack. Mistakes were made at first by taking too high a percentage of hardened fat until experience taught a successful blending of 30 to 50 per cent of the latter with 70 to 50 per cent of a softer-bodied fat or oil. A fat composition of 50 per cent of the hardened oil, 20 per cent palm-kernel oil or coconut oil and 30 per cent peanut oil has proved to be a splendid formula for white soaps. The very fact that this hardened whale oil had to be blended with soft-bodied oils and fats in order to produce a soap easily soluble in water made the manufacture of rosin soaps that much easier. In European countries soapmakers do not use such high percentages of rosin in their laundry soaps as we do here, and a percentage of 40 per cent rosin is considered there extremely high.

Below is a formula of a rosin soap, typical of the German pale yellow soaps:

1500 lb. hardened linseed oil (linolith) fatty acids.
500 lb. peanut oil
700 lb. soft-bodied grease
300 lb. palm-kernel oil
<hr/>
3000 lb
1200 lb. rosin = 40 per cent
<hr/>
4200 lb.

Prior to the advent of the hydrogenation process, Schuck observes, linseed oil was used almost entirely for soft potash soaps and whoever tried to use it in laundry soaps, even in very limited quantities, was sadly disappointed. The trouble resided not alone in its soft-bodied character, but in the fact that the unsaturated linolic and linolenic acids produced in a short time yellow and brown spots on the surface of the soap and made it quite unsalable. Here also,

\* Soap Gazette and Perfumer, 1914, 419.



says Schuck, hydrogenation has done wonders. It changed the physical character of the oil entirely. Consider, on the one hand, the fast drying, soft-bodied, yellow and fishy-smelling linseed oil and, on the other hand, the hardened product, white, hard, non-smelling and suitable for any kind of soap, be it laundry or toilet soap. Experience has proven that even on long aging the characteristic yellow and brown spots of the linolic and linolenic acids do not appear on soaps made from hardened linseed oil.

Soaps made from hardened linseed oil showed at first a slight reddish discoloration, but this was rather the fault of inexperienced settling of the soap than of the fat itself. The brittleness of the soap which the first batches showed was subsequently overcome by a proportionate blending of linolith with peanut oil or castor oil. Castor oil soaps have the peculiar faculty of remaining liquid even if highly concentrated and for that reason are splendid supplementary soaps to those made from hardened fats. The percentage of castor oil need not exceed 15 per cent to result in a soap which is easily soluble in water and which possesses very good lathering qualities. Schuck concludes with the suggestion of a prophecy that the time may not be so far off when hydrogenated raw materials will be as universally used in this country as abroad and that fore-knowledge is very often half of the battle.

At one time, **Knorre** \* observes, it was thought that hardened oils would displace all other fats in the soap industry but the difficulties encountered with hydrogenated fish and whale oil in soap making changed this view.

Soaps made from the latter fats were "stone-hard," very brittle, were pressed with difficulty and lathered poorly. The odor of the soap was unpleasant, especially after keeping for a considerable time, the initial white color changed to yellow, yellowish red or brown and on the surface of the cakes varnish-like exudations of strong odor appeared. Samples of grained soap of a neutral character, firm consistence and good tallowy odor, prepared from hardened train oil on keeping for a few weeks in a closed box, changed materially in this time. The cakes were fissured, the color was a rusty brown and the odor was disagreeable. For these reasons hardened fish and whale oil can be recommended for use in soaps only in moderate amounts. The allegation that these hardened fats serve as substitutes for palm kernel and cocoanut oil is without support.

Fatty acids can be obtained from hardened fats by autoclave, Twitchell or ferment cleavage. In the autoclave process, zinc powder is the best cleavage agent because the resulting fatty acids are the least discolored. When decomposing the products of the autoclave treatment with sulphuric acid, agitation is secured by means of a current of air. The glycerine obtained is of good quality and contains 0.2 to 0.5 per cent ash. It may be rendered entirely white by treatment with blood charcoal in vacuum.

In the table below, the properties of the fatty acids obtained from several grades of hardened fish and whale oil are given by Knorre; the names by which these products are sold in the German market being used.

The direct pressing of the fatty acids of Candelite is not recommended. It is better to mix Candelite and tallow or refined bone fat, subject to cleavage

\* Seifen. Ztg., 1914, 806.

PROPERTIES OF THE FATTY ACIDS OF HARDENED FISH AND WHALE OIL \* (KNORRE)

Trade Name.	Appearance.	Loss on Drying.	Ash.	Unsaponifiable.	Non-fatty Material.	Saponifiability.	Acid Number.	Saponification Number.	Ester Number.	Neutral Fat, Per cent.	Iodine Number.	Visc. Test, ° C.
Talgol fatty acids	Tallowy hard mass. Snow white	0.21	0.01	0.12	0.34	99.66	187.6	203.0	15.4	7.8	69.0	42
Olinit fatty acids	Odor, sweet. Hard	0.15	...	0.31	0.46	99.54	186.1	208.8	22.7	9.1	61.1	43
Talgit fatty acids	Crystalline. Snow white	0.21	0.01	0.49	0.71	99.29	187.1	206.1	19.0	9.0	40.2	41.2
Talgol-extra fatty acids	Very hard. Tallowy	0.31	0.03	0.51	0.87	99.13	189.3	208.9	19.6	9.9	54.3	49
Candelite fatty acids	Tallowy	0.35	0.08	0.26	0.69	99.31	191.0	204.1	113.1	6.8	20.3	49.6
Candelite-extra fatty acids	Hard crystalline mass	0.15	0.10	0.31	0.56	99.44	193.0	209.1	16.1	8.4	8.9	56.1

\* Seifen, Ztg. 1914, 971.

and then mix the fatty acids with olein or runnings from hot pressing in order to improve the pressing operation.\*

As already mentioned, hydrogenated oils have been receiving considerable criticism by the soap makers because of the relatively low lathering qualities of soaps prepared from these oils.

The addition of a large proportion of hydrogenated oil to the soap batch is, therefore, precluded. In order to secure a free lathering soap from hydrogenated fatty material, the author † first polymerizes the oil and then subjects it to the hydrogenation process. The polymerization is carried out by protracted heating preferably in the absence of air until the iodine number has been reduced to as low a degree as is feasible. This reduction depends upon the oil which is being treated. Fish or whale oil may have the iodine number readily reduced by polymerization to about 80 or 90. Such products usually still possess a fishy odor and by hydrogenating to an iodine number of 40 or 50 the odor is eliminated and, in some cases, the taste becomes fairly bland. The author has prepared soaps from such products and finds them to possess relatively good lathering properties and to yield soaps in other respects of quite satisfactory quality.

Further details of the joint result of polymerizing and hydrogenating a fatty oil are described below.‡

Fatty acids and unsaturated oils such as the glycerides containing more especially two or more double bondings or olefine groupings are capable of polymerization at elevated temperatures resulting in a thickening of the oil due not so much to the formation of stearine as to the formation of oil complexes by the union of oil molecules one with another, usually denoted by a profound reduction of the iodine number and other changes. In this manner castor, fish, whale, cotton, corn, linseed, rape and tung oil and the like may be polymerized to differing degrees and by such polymerization a thickening of the oil usually occurs which produces a body of viscosity that enables one to obtain by hydrogenation, a product containing a fatty derivative of good texture or consistency. The product may be used in making lubricants, or may be sulfonated by treatment with sulphuric acid or soaps may be prepared by saponification with alkalis.

When catalyzers such as nickel oxide are employed, it is preferred first to polymerize the oil at about 250° C. and then to reduce the temperature and harden by means of hydrogen or hydrogen and oxygen at a temperature around 200° C. When using palladium the temperature may be much lower.

Hardened or hydrogenated oil produced by simple hydrogenation is not capable of yielding soaps having as free lathering qualities as often as desired, while some grades of the polymerized and hardened hydrogenated oil show superior lathering qualities when converted into soap.

To remove the odor from fish and whale oil by hydrogenation requires a considerable conversion to stearine. Usually it is necessary to reduce the iodine number of fish oil to 40 or 50 in order to convert the unsaturated bodies such as clupanodonin which are supposed to be more or less odor-producing into more

\* Seifen. Ztg., 1914, 812.

† U. S. Patent No. 1,151,002, August 24, 1915.

‡ U. S. Patent No. 1,178,142, April 4, 1916.

saturated or entirely saturated bodies rendering the oil free from disagreeably fishy odor. But hydrogenation to this point produces so large a proportion of stearine which lathers freely as a soap only in very hot or boiling water that the product when used with cold or slightly warm water is deficient in lathering and consequent detergent properties. By polymerization the property of cold lathering existent in the soaps produced from normal fish oil is to a considerable degree present in the polymerized oils and any further hardening which may be desired and which is secured by hydrogenation does not impair these lathering qualities to any material degree in connection with the production of fats for making hard soaps. Hence, polymerization enables the production of fats from oils and fats of a thickened or hardened product without the necessity of carrying hydrogenation forward to such a degree that the lathering properties of the soap are seriously impaired.

The following procedure will serve to illustrate the foregoing: Whale oil was heated in an atmosphere of carbon dioxide for sixteen hours at a temperature between 250° and 270° C. The final product was viscous and the fishy odor was largely eliminated. The iodine number of the oil before heating was 135.5 and that obtained after heating had an iodine number of 89.7. The polymerized oil was treated with hydrogen in the presence of nickel material as a catalyzer and a product was obtained which did not appear to have any very definite melting-point. Changes in temperature between quite wide ranges did not appear to affect the consistency very materially. It melted completely at about 37° C. and the iodine number was found to be 65.9. A quantity of the whale oil which had not been polymerized was hydrogenated under the same conditions and soaps prepared from both the products by saponification with alkali under like conditions. The soap obtained from the hydrogenated whale oil had almost no lather in cold water, while the polymerized and hydrogenated product gave a copious lather in water of the same temperature. The fats as well as the corresponding soaps were free from any fishy odor. It appears to be an approximately correct statement that the lathering qualities of a soap depend on the melting-point of the fats from which it is made. A soap made from oleic acid lathers rather easily in cold or slightly warm water, while that made from stearic acid requires a temperature of nearly 80° C. to develop a satisfactory lather. The absence of any definite melting-point in the particular product illustratively given herein possessed no very definite melting-point, as stated and was capable of lathering freely in cold or tepid water. Soaps prepared from oils which are highly unsaturated such as linseed oil or fish and whale oils are often prone to discolor due to the tendency to oxidation of some of the unsaturated constituents. If the oil is hardened to a point where discoloration is not liable to take place and undesirable odors are removed the lathering qualities are impaired, while by polymerizing a goodly proportion of the components which tend to bring about oxidation are eliminated without any material detrimental influence on the lathering properties and by final treatment with hydrogen a sufficient amount of consistent material is obtained to give the requisite body or firmness to the soap. The amount of hydrogen required is less, which is a saving in cost.

Polymerization of unsaturated oils by the action of ultraviolet light in the presence of reducing gases is noted by Ellis.\*

\*U. S. Patent No. 1,180,025, Apr. 18, 1916, and 1,179,414, Apr. 18, 1916.

The hydrogenation process enables olein (oleic acid) to be prepared in two ways according to Dubovitz \* either by treating hydrogenated fatty acids of a titre of 40 to 46 in the usual way to separate stearine and olein or to hydrogenate cheap oil of high iodine number to bring the iodine number to about 80 or 90 or approximately that of olein, and saponify this product. The resulting olein contains only a few tenths of a per cent of unsaponifiable matter and a few per cent of neutral fat. The liquid fatty acid contains highly unsaturated components in spite of the iodine number of 80 to 90.

The application of hardened oils in the candle industry is noted by Bontoux † who states that the operations of pressing or distillation, impose a limit on the degree of hardening practicable.

In splitting fats with aromatic sulpho-fatty acids, the color of the resulting product is improved by using hydrogenated castor oil, containing hydroxyl, for preparing the dissociating agent. One part each of hardened castor oil and naphthalene are ground to a powder and treated with four parts of commercial sulphuric acid at a temperature below 20° C. The resulting product is poured into eight parts of water and the upper layer which forms is collected and used as a fat splitting agent.‡

Formulas for the production of white-grained soap employing hardened linseed and fish or whale oils are given in *Seifensieder Zeitung*, 1914, 644, 705 and 931. A soap or soap powder of great detergent power is described in the same journal, p. 511.

A grade of hardened linseed oil (linolith) made for the German market produces a toilet soap base of pure white color § see also *Seifensieder Zeitung*, 1914, 540, for approved formulas by Schaal employing hardened fish oil. On page 543 Berge gives a number of soap stock formulas using Linolith, Talgol or Candelite.

Timely substitutes for coconut oil soaps are discussed by Schaal. || At least 40 to 50 per cent of coconut oil must be used to secure easy saponification, rapid lathering and general appearance. Four formulas are given using tallow, hardened oil, hog fat and castor oil in varied proportions.¶

In Germany, during the war, hydrogenated fats have played an important part in soap making. The lack of lathering power in soaps made from hardened oil can be corrected, according to Davidsohn \*\* by additions of coconut

\* Seifen. Fabrikant, 1915, 137 and 157, *Seifen. Ztg.*, 1915, 459.

† *Matières Grasses*, 1914, 4194; *Seifen. Ztg.*, 1914, 987.

‡ German Patent 298,773, Vereinigte Chem. Werke, A. G.; American Perfumer, 1918, 382.

§ Schaal, *Seifen. Ztg.*, 1914, 600.

|| *Seifenfabr.*, 1914, 1158.

¶ *Chem. Abs.*, 1915, 389.

\*\* *Chem. Ztg.*, 1915, 330.

or palm-kernel oil, or rosin. A soap prepared from 50 parts hardened linseed oil, 30 parts cocoanut-oil fatty acids and 20 parts of rosin exhibited good lathering properties. A cold process soap made from 40 parts hardened oil and 60 parts cocoanut oil possessed an excellent appearance and the lathering powers were good.

The advantageous utilization of hardened fats in soap-making, specially during the war, is discussed in *Seifensieder Zeitung*, 1914, 1109. Various formulas are given. For methods of making soft soaps from these materials, especially Talgol and Krutolin, see *Seifensieder Zeitung*, 1914, 1130.

The commercial application of the hydrogenation process to the French soap-making industry is described by Gurney.\*

In connection with considerations involved by the war, it has been pointed out † that the *Oelwerke Germania* is owned by the firm of Jurgens, which is operated by Holland and British capital. A response to this comment appears in *Seifensieder Zeitung*, 1914, 1073.

At an exposition in Magdeburg ‡ the *Oelwerke Germania* of Emmerich exhibited a series of hardened oils, viz.; Durotol M.P. 60°, Coryphol M.P. 80° C., Talgol, Talgol extra, Linolith, stearine and olein from Talgol extra, crude glycerine from linolith, stearine candles from Talgol extra and various soaps made from hardened fats. One of these was a toilet soap containing 43 per cent of hardened linseed oil. (Linolith.)

The Oil, Paint and Drug Reporter § reviews the progress of hydrogenation during 1913 and notes that because of the relatively low price of linseed oil in Europe this oil has been more generally hardened for soap makers than other oils. Abroad, cottonseed oil is not hardened extensively, except for edible purposes. Small quantities are being hardened for margarine, and this will probably be an important business. The total capacity of the European hardening plants for 1914 is put at 1,375,000 barrels (400 lb. each), but not more than half this amount was made in 1913. In the U. S. the output for 1913 is put at 500,000 barrels and is rapidly increasing.

During 1917 an extraordinary demand from soap and candle makers kept the white and yellow grease stearine market at Chicago strong throughout the year. || Although the record-breaking prices which prevailed during the year was a stimulant to production, supplies of stearines were never burdensome during 1917. Early in the year oleo stearine attracted a good premium over tallow due to the strong demand from compound makers, but later in the year the demand from this source waned somewhat when the hydrogenation of bean oils for oleo stearine was carried out extensively. The substitution of the hydrogenated bean oils for oleo stearine reduced the demand for stearine on the part of compound makers to a minimum.

\* Chem. Trade J., 55, 187.

† Seifen. Ztg., 1914, 1030.

‡ Seifen. Ztg., 1914, 863.

§ July 20, 1914; J. S. C. I., 1914, 837.

|| O. P. & D. Reporter, 1918, 71.

Hydrogenated coconut oil obtained from Oelwerke Germania of Emmerich, was used by **Schrauth**\* in preparing certain special soaps; *one grade of which contained oxycyanide of mercury*. The lack of lathering properties of hardened oil soap is overcome by the addition of castor oil or turkey-red oil (5 to 10 per cent).†

The cost of hydrogenating fatty oils according to **Bontoux**‡ at first was figured at 7 to 8 francs per hundred kilos of oil but at the present time certain patent owners are guaranteeing a maximum cost of 3 to 4 francs per hundred kilos, depending on the nature of the oil and its intended use.

**Schrapinger**§ has studied the hydrogenation of Chinese wood oil in order to throw some light on the structure of wood oil fatty acid. Reduction could not be carried out by the method of Erdmann and Bedford|| because the acid polymerizes under the conditions imposed.

Accordingly Schrapinger used the method of Paal¶ (palladium-hydrosol as hydrogen carrier), and the modification by A. Skita (higher pressure, for the purpose of accelerating the reaction).

The wood-oil acid to be reduced was dissolved in 30 cc. of alcohol. The palladium chloride was dissolved in 50 cc. of boiling water; 0.5 g. of gum arabic was also separately dissolved in 50 cc. of water. The two solutions were mixed after cooling, and the alcoholic wood-oil acid solution was added; enough ether and alcohol was then added so that a uniform liquid was obtained. Hydrogen, under one atmosphere pressure, was then forced into this mixture, and the closed vessel shaken during the process. In two separate experiments, the sodium salt, as well as the free acid, was reduced. It was found that the sodium salt reduces better than the acid itself, owing to the greater solubility of the sodium salt in aqueous alcohol, thus eliminating the possibility of coating the colloidal palladium particles by precipitated acid.

After the reaction was finished, the solution was raised to boiling, then filtered and finally evaporated. The residue was dissolved in hot water, and acidulated with hydrochloric acid. The precipitated acid was recrystallized from alcohol, possessed a melting-point of 69° to 69.5° C. and showed the following composition:

1. 0.2138 g. substance gave:  
0.5969 g. CO<sub>2</sub> corresponding to 0.1627 g. C.,  
0.2386 g. H<sub>2</sub>O corresponding to 0.0266 g. H.
2. 0.1941 g. substance gave:  
0.5424 g. CO<sub>2</sub> corresponding to 0.1479 g. C.,  
0.2135 g. H<sub>2</sub>O corresponding to 0.0238 g. H.

\* Seifen. Ztg., 1915, 17, 371; Soap Gazette and Perfumer, 1915, 424.

† Seifen. Ztg., 1914, 992.

‡ Matières Grasses, 1914, 4194; Seifen. Ztg., 1914, 987.

§ Dissertation, Karlsruhe, 1912; Stevens and Armitage, China Wood Oil, Vol. II, Part 2, 2770.

|| Ber. 1909, 42, 1324.

¶ Ber., 1905, 38, 1406, 2414; 1907, 40, 2209; 1908, 41, 2273, 2282.

Calculated for  $C_{18}H_{34}O_2$  C=75.98 per cent, H=12.76 per cent,

Found C=76.09 per cent, H=12.44 per cent,

C=76.19 per cent, H=12.26 per cent

The product obtained, therefore, was stearic acid, whereby it was proven that elaeomargaric acid is an acid with a simple (straight) chain. Yield: 63 per cent of the theory.

A procedure given by **Levinstein**\* relates to the production of compounds from hydrogenated saponifiable fats or oils and to the production therewith of compositions from waxes, fats, oils, or the like, which are soluble, miscible, or emulsifiable in water without the addition of alkali.

The compositions obtained are stated to be valuable in the preparation and treatment of leather, and in the textile industries, as special finishes.

In carrying this method into effect, hardened oils obtained by the hydrogenation of saponifiable fats or oils, such, for example, as hardened fish oil or hardened linseed oil, are treated under certain conditions with sulphuric acid. The sulpho compounds so obtained have the property of making mineral and other waxes, oils, fats, or the like soluble, miscible or emulsifiable in water.

In order to obtain these sulpho compounds, hardened linseed oil, for example, is selected, and after melting is treated with sulphuric acid until a sample from the mass gives an emulsion with water, or until a washed sample practically dissolves in ammoniacal water. The mass is then poured into water previously heated to 30° C., when the sulpho compound will separate in the form of a white pulpy mass.

The following is an example of how a sulpho compound may be produced and how such compound may be used to produce a soluble composition with mineral wax:

One hundred parts of hardened linseed oil are melted and then cooled to about 35° C. under agitation. Twenty-five parts sulphuric acid (100 per cent  $H_2SO_4$  monohydrate) are then added gradually and the temperature is kept between 40° to 45° C. until a washed sample is practically soluble in hot water. The whole is then run into a salt solution (10° Tw.) which has been heated to a temperature of 30° C., is well stirred, and then allowed to settle, after which the salt water is drawn off. The washing with salt water is again repeated until the mineral acid has been removed, or the mineral acid may be neutralized with alkali. The sulpho acid of hardened linseed oil, thus obtained, when melted and mixed with equal parts of paraffin wax gives a composition which is practically soluble in hot water without the addition of alkali.

The hardened oils can be sulphonated when mixed with oils or greases, but the property possessed by the product of making waxes miscible or soluble or emulsifiable in water without neutralizing the sulpho acid or without any addition of alkali, appears to be to some extent diminished.†

Experiments on the catalytic hydrogenation of two kinds of oil from the French colonies, namely, "Karite" of French West Africa and

\* U. S. Patent No. 1,185,414, May 30, 1916.

† British Patent No. 16,890, July 16, 1914; J. S. C. I., 1915, 913; Chem. Abs., 1916, 288.



"Aouara" of Guiana have been carried out by Heim and Hebert.\* Karite (*Butyrospermum parkii*) butter and fat of Aouara nuts mixed with catalyzer were placed in flasks and pure dry hydrogen was passed through at a pressure of 1 to 2 cm. of mercury above atmospheric pressure. The process was carried out at 50° and also at 180° to 200° for twelve hours with constant agitation. As catalyzers reduced platinum in the proportion of 1 per cent and reduced nickel, 5 per cent, were used. At the end of the process the mixture was dissolved in benzine and the fat obtained by evaporation. Results are given in the following table:†

Treatment.	KARITE BUTTER.		FAT OF AOUARA NUTS.	
	Melting-point	Iodine Value	Melting-point.	Iodine Value.
Initial . . . . .	32°	65.6	30°	9.5
After hydrogenation with Pt. at 50°. . . . .	35°	57.6	30°-31°	9.2
After hydrogenation with Pt. at 180°-200°. . . . .	67°-68°	16.0	32°	8.1
After hydrogenation with Ni at 50°. . . . .	34°-35°	48.0	30°-31°	9.0
After hydrogenation with Ni at 180°-200°. . . . .	69°-70°	9.6	32°	6.7

Padoa and Dalla ‡ describe a process of deodorizing and decolorizing chrysalis oil by passing a current of air or hydrogen or a mixture of these gases, at 140° to 250°, through the oil, to which may be added a catalyzer. The decolorization of the oil, which becomes brown as a result of the treatment, is effected by shaking with dichromate and H<sub>2</sub>SO<sub>4</sub>. The oxides of nickel, cobalt, iron, manganese, copper, lead, cerium, etc., are specified as suitable catalyzers.§

Schmitz || reports that the hydrogenation of crude naphthenic acids, employing a catalytic agent, did not affect the odor or properties of these acids.

#### LUBRICANTS CONTAINING HARDENED OIL

¶ Krist ¶ has supplied the following formulas which he states were furnished by Georg Schicht A.-G., Aussig.

\* Ministère des Colonies, Bull. de l'Office Colonial 50,8, 238-44, 1915; Bull. Agr. Intelligence 6, 1247-8, 1915.

† Chem. Abs., 1916, 1106.

‡ Italian Patent No. 138,942, May 5, 1914; Chem. Abs., 1915, 2822.

§ See also Tsujimoto, Chem. Ztg., 1914, 110.

|| Mat. grassea, 7, 4115; J. S. C. I., 33, 684.

¶ Seifen. Ztg., 1913, 776.

## 1. Very consistent and uncolored compound for heaviest types of machinery.

- 40 Kilos hardened oil (Talgit);
- 3 5 Kilos caustic potash solution 50° Bé;
- 13 Kilos caustic soda solution 37° Bé;
- 75 Kilos American mineral oil sp. gr. 0.870.

## 2. Colored compound for heavy machinery.

- 40 Kilos hardened oil (Talgit);
- 3 5 Kilos caustic potash solution 50° Bé;
- 13 Kilos caustic soda solution 37° Bé;
- 150 Kilos mineral oil (0.870);
- 15 g. Chinolin yellow (fat soluble).

## 3. Grade for lighter machinery.

- 40 Kilos hardened oil (Olinit);
- 3.5 Kilos caustic potash solution 50° Bé;
- 13 Kilos caustic soda solution 37° Bé;
- 150 Kilos mineral oil (0.870);
- 20 g. Chinolin yellow (fat soluble).

Brooks \* describes a process of manufacturing hydrogenated rosin having many of the properties of common rosin such as solubility in varnish solvents and saponifiability or soap-making properties but differing from ordinary rosin by possessing a substantial stability and diminished oxidizability as evinced by giving a lessened absorption of iodine or bromine. Varnishes can be prepared from the treated rosin which do not crack and fissure upon standing and soaps or soap compositions, sizes, etc., may be prepared from it which do not yellow with age.

It is stated that ordinary rosin or colophony, although often used in the manufacture of cheap low-grade varnishes, enamels and the like, gives varnishes which, in time, crack and fissure or "craze." Rosin makes an unusually lustrous varnish film, and if it were not for this lack of permanence it would be a highly desirable varnish resin. In other uses, rosin displays the same tendency to alteration and deterioration with time. Rosin soaps are not permanent but become yellower and harder on keeping. In one of the most extensive uses, sizing paper, the same tendency obtains. This lack of permanence is stated by Brooks to be largely due to the fact that rosin is an unsaturated body and, therefore, tends to oxidize when exposed to air, in the way in which it is exposed in a varnish film, in a body of soap or as the sizing in paper. In the case of rosin size in paper the oxidation not only affects the size itself but the paper as well; probably because of the development of peroxide, formic acid, etc. Rosin-sized paper, particularly if exposed to light and air, in time becomes friable and yellow. By combining or saturating the rosin with hydrogen, a material is obtained which displays all the valuable properties of rosin as regards the making of high luster varnish films and the preparation of soap while it no

\* U. S. Patent No. 1,167,264, January 4, 1916.

longer has the undesirable property of lack of permanence or stability when exposed to the air. This stabilized rosin or colophony when converted into varnishes is claimed to give a high-grade varnish in lieu of the ordinary low-grade article; a varnish film which is permanent in air, and at the same time of good appearance. It is also adapted to make a better grade of soap and a higher class, more permanent paper size.

Brooks observes that abietic acid, or the acid of rosin, appears to hydrogenate in stages, there being a first absorption of hydrogen which is more energetic than the later absorption. This first, easily hydrogenating stage corresponds to the highest oxidizability and if the hydrogenation be carried only to the end of this first stage the rosin loses most of its alterability in air.

While the addition of hydrogen to the rosin may be performed in many ways: a simple method of procedure is to reduce the rosin to a fluid state by heat, stir in 3 per cent of freshly-reduced nickel and expose the mixture to an atmosphere or current of hydrogen. Any suitable stirring or agitating means may be used to produce intimate contact of the mixture of rosin and catalyst with the hydrogen gas. A temperature of 180° to 230° C. is suitable for this operation. The progress of the reaction may be followed by watching the gauge pressure where the operation is performed under pressure. When the pressure, as indicated by the gauge, ceases to diminish with comparative rapidity, that is, the rapidity of absorption of hydrogen slackens, the first stage of saturation is over. After this time there will be a slower diminution of pressure. The treatment may be carried to a point where the iodine absorption shows no further substantial reduction on continuation of the treatment or to the point where the iodine number disappears altogether.

Instead of using nickel, other metals such as cobalt, copper or iron may be employed, but these other metals are not quite as effective as the nickel. Whichever metal is used it is best reduced from an oxide formed from its nitrate, reduction being by a current of hydrogen at a low temperature; a temperature not markedly in excess of 200° C. and advantageously lower. Instead of using these metals, their oxides may be employed, but in this event it is desirable to perform the treatment with hydrogen at a somewhat higher temperature, say about 240° C.

The catalyst may be used with any of the usual carriers such as kieselguhr, or asbestos, etc., to increase the contact surface.

"Impregnation" with hydrogen may usually be accomplished in about three hours at 200° C., using freshly reduced nickel.

In lieu of simply melting the rosin, a solvent may be used as a vehicle for the rosin and catalyst; such as alcohol or a good grade of kerosene.

Instead of using the stated metals, or their oxides, colloidal palladium (or palladium chloride) or other platinum group metal, may be used. Palladium in the colloidal or spongy condition is stated to be an advantageous catalyst. In using colloidal palladium, hydrogenation may be performed at the ordinary temperature or slightly higher, the rosin in this case being maintained in a fluent condition by the use of an appropriate solvent, such as alcohol, benzol, gasoline, toluene, etc. Colloidal palladium may be directly formed in or added to the rosin solution or it may be produced in an oily carrier and then added to the solution of rosin. Or a water solution of colloidal palladium may be agitated with a solution of rosin in a suitable solvent in the presence of hydrogen until the desired degree of saturation is effected.

Similar results to those given by colophony may be obtained upon hydrogenation of many other resins known as varnish "gums" and in use for making varnish. It is claimed that the hydrogen treatment much improves their stability and quality. Among other resins which may be improved by hydrogenation are Pontianak and guayule resin.

When using iodine to control the reaction, a convenient form of test is the Hanus method of determining the iodine number. Brooks states that ordinarily he carries on hydrogenation till the resultant product shows an iodine value of 20 or less by the Hanus method.\*

#### HYDROGENATED OIL IN THE TANNING INDUSTRY

Hydrogenated oils are now being used by tanners for stuffing leather and other purposes. Fish and whale oil are especially suited for this purpose. A product low in fatty acids is desired, as any large amount of free, fatty acid is regarded by the tanner as likely to cause the leather to spue.

A paper by Lombard before the American Leather Chemists' Association, Chicago, October 30, 1914,† and presented by Dr. Rogers contains the following discussion on the hydrogenation process and refers particularly to leather manufacture.

It is everywhere known that those industries which work up fats have been seriously upset for many years by the considerable advance of prices of raw materials. The rapid development in the manufacture of fats for nourishment, especially, has made solid fats so scarce and expensive that the soap industry which absolutely requires solid fats for the manufacture of solid toilet and household soap, have found it very difficult to get the necessary raw materials. As there are still large quantities of liquid fats obtainable at quite low prices, it has consequently become a necessity to find a chemical method for the transformation of the liquid raw materials into solid ones. The problem has been solved by the catalytic method of hardening fats.

The liquid fats differ from the solid ones by the low percentage of hydrogen of their fatty acids, by the unsaturated character which besides the liquid condition involves still other properties, by the tendency to rapid oxidation in open air, by the dark coloring and by the disagreeable fish odor of the highly unsaturated fish-oil fatty acids which hampers the possibility of employing fish oils.

For more than fifty years the problem of hardening fats occupied chemists and manufacturers, but none of the many processes which have been suggested could be carried out in practice.

With the development of physical chemistry, the science of the "katalysatoren" has got footing, and after it had been shown by the experiments of the French savants Sabatier and Senderens, that by the aid of nickel in a fine state of subdivision it is possible to join hydrogen to unsaturated compounds, W. Normann found that unsaturated fats or fatty acids, in which finely-divided nickel was suspended, could be made to unite with hydrogen. In Germany the process of Normann for a long time did not attract any attention, but it was taken up

\* See also U. S. Patent No. 1,249,050 to Ellis.

† J. Am. Leather Chemists, Association, 1915, 80.

by the English firm of J. Crosfield & Sons, and perfected in a few years to an important technical process which supplied in 1906 many tons a day.

The German patent passed on to the Naunloozee Venootschap Anton Jurgens, who established in 1911 the Germania Oelwerke, where to-day 100 tons of liquid fat, mostly fish oil, are being hardened every day.

A great number of patents have been asked for the employment of the nickel method, which, however, in Germany are all dependent on the Normann patent. The most known of these processes is the one of Wilbuschewitsch. After an arrangement with the Germania Oelwerke they now use their process for the manufacturing of hardened oils for food purposes.

Besides the nickel method, another one developed from the experiments of Paal, which used palladium as a catalyzer. The addition of hydrogen in this case is done more quickly and at a lower temperature, and the products are very satisfactory, but in view of the high price of palladium competition with the nickel method is impossible.

Great attention has been called to a process of Erdmann and Bedford, in which oxide of nickel is substituted for nickel. The oxide of nickel seems to be more insensible toward the soilings of the oil and the hydrogen than the metal in fine distribution. This process has been also perfected in England. A factory in Germany, the Oelwerke Hydrogen, will start manufacturing within a short time. A heated dispute, which is not yet decided, is carried on about the question whether in the Erdmann process also, nickel is the effective catalyzer, as is supposed by Normann, or whether the conception of Erdmann is right, who says that the oxide of nickel is being reduced to suboxide, which acts as a catalyzer. A German patent for the nickel oxide method has just been granted, after the English patent has been in force for several years.

A number of other processes are based upon nickel compounds, which, during the treatment with hydrogen are transformed to nickel. The method of Winnem-Higgins, for the exploitation of which the Fettraffinerie A. G. at Brake has put up a factory, is using especially formate of nickel. This method is also closely connected with the one of Normann.

The hardened fats, hardened fish oils, linseed oil and cottonseed oil are to-day used to a very large extent for soap manufacturing, on account of the superior foaming properties, in conjunction with other fats.

For the manufacturing of edible fats, the hardening of fats is of utmost importance, because by the aid of this method it is possible to use vegetable oils in place of animal fats, after the former have been hardened to the proper melting-point.

Manufacturers, however, on principle, do not use hardened fish oil for food products, in order not to give the producers of natural butter any more topics to agitate against margarine, although the production of butter in Germany is not sufficient by far to cover requirements.

In a general discussion which followed, Lombard stated that the reason he wanted to call the Leather Chemists' Association's attention to this product which he had brought over from Germany, was, that in his trip to Germany he visited many tanneries, and saw these products in actual use, especially solidified linseed oil, of which they used a good deal in dressing patent leather. They were also using quantities of solidified cottonseed oil. He saw it being used for replacing the old-fashioned saponified linseed oil, which they used as a top dressing in their

patent leather. And they have practically replaced the raw linseed oil they previously used with this solidified linseed oil. Cox said some experiments had been carried on with a hydrogenated linseed oil from England. It can be used as a fat-liquor up to about 9 per cent, and still japan can be put on top of it without degreasing it, and the japan not loosened. Yocum inquired if it were possible to use hydrogenated oil to the extent of 9 per cent of the weight of the leather and still be able to japan, and in reply to this Cox stated that the hydrogenated oil is sulphonated, which affords a solid product of comparatively high melting-point and could be used in a leather which is non-degreased. Leather will carry 9 per cent of the oil and show no objectionable grease. Faust inquired if Lumbard had visited any harness leather tanneries and whether hydrogenated whale oil was being used as a stearine substitute in Germany. To this Mr. Lumbard responded that it was not being used exactly as a stearine substitute, but to replace many of the oils such as moellon. In conjunction with stearines and tallow it has better carrying qualities, absorbing and carrying the greases in better, so the tanners stated, and it leaves the flesh very clean. It has been adopted for dressing, for instance, on satchel, bag and case leathers, because in dressing with it, it does not run. It is about of the consistency of a very heavy butter, and when it is subjected to heat becomes limpid. They then mix it with a little sulphonated oil to make it flow and when the leather is hung on the hooks they claim that it does not drip, that the absorption of the oil is clean and clear, and that it does not run to the skirts as so many free-running oils do. So on all those harder leathers it has been used to a great extent, and also on harness leather. Cox stated that with this oil it is possible to make an emulsion and take sole leather of very light color, dip the leather into it, and have the leather dry out without any loss in color. Saxe made the inquiry whether fish oil or vegetable oil was preferred for patent leather and Lumbard stated that fish and linseed oil were preferred to cottonseed oil, the reason given being that the cottonseed oil hardened more than other oils. The most satisfactory oil of all is the hardened fish oil. In answer to an inquiry by Mr. Yocum regarding the possibility of sulphonating the oil and then hardening it to bring it up to the requisite condition, Lumbard stated that in Germany it was the custom to blend hardened oil with sulphonated oil to produce an emulsion and use it in that form as a fat liquor. Cox stated that it was perfectly possible to take one part of the sulphonated hydrogenated product, combine it with four parts of a fat such as stearine, melted, and have it form an emulsion, then put the leather in it, hang up while still wet, and the stock would come out without any discoloration. Lumbard stated that what interested most of the German tanners in this product is the fact that when combined with the sulphonated oil, the linseed oil being a very drying oil, will carry into the leather and it leaves the surface absolutely clean and free from any fats that may come up during the process of baking in the ovens. Ordinarily unless the leather is degreased, the first coat has a tendency to peel. They do not experience any of those difficulties in the use of this hardened linseed oil. Yocum inquired if hydrogenated linseed oil still retained the property of drying and if it could be boiled into a sweetmeat or varnish, to which Lumbard responded that they did not use the hydrogenated linseed oil for boiling varnish. When this oil is blended with a sulphonated fish oil, which they use considerably in conjunction with it, he said it seems to lose considerable of the oxidizing effect, that the original linseed oil would have. It leaves the surface very clean. The oil does not flow out, it does not come out in the heat of the ovens, especially under

a temperature of 140 degrees, to which they subject leather in their ovens. They follow up the primary coat with a collodion coat, and it is said that the collodion coat adheres to the sweetmeat coat better where they use the solidified oil than where they use the free oil in fat-liquoring.

#### GREASES FOR STUFFING HARNESS LEATHER, BELTING AND OTHER HEAVY LEATHER

For stuffing heavy leather, such as belting and harness leather, various greases are employed, tallow being frequently used for the purpose. The heavier grades of mineral oil are sometimes added to the stuffing grease. Leather of this character requires from 10 to 30 per cent or more of stuffing fat and the general shortage of low priced fats renders any new source of fatty material of interest. Hence tanners have experimented extensively with hydrogenated oils, with generally promising results. The most useful fat is one having a melting-point of about 125° F. and containing not in excess of 2 per cent of free fatty acid. With higher percentages of fatty acid there is danger that the leather may spue.

#### PREPARATION OF FATTY ACIDS

Starrels \* prepares fatty acids by hardening a fatty oil to a high melting-point, as, for example, to about 60° or 62° C., and an iodine number of from zero to 2 and thereby substantially completely converting the olein into stearine, also forming various isomers of high melting-point.

The material is saponified by the Twitchell process or any of the other fat-splitting processes yielding glycerine and high melting-point fatty acids. The latter mixture is then dissolved in a solvent medium, as, for example, alcohol or gasoline, and, on cooling, the free fatty acids are separated in a state of purity, leaving in solution the greater part of the coloring agents. An example is the following: Corn oil was hydrogenated, using nickel catalyzer, until the melting-point was about 62° C. It was then subjected to the Twitchell process and the fatty acids obtained. These were brown in color. Approximately equal parts of denatured alcohol and the fatty acid were incorporated and heated to form a homogeneous solution which takes place rather readily at temperatures approaching the boiling-point of alcohol as the fatty acid is relatively soluble in alcohol. The solution was cooled until practically all of the fatty acid had separated, when the material was pressed and a brown extract containing the hydrocarbons and coloring matters was removed leaving a white fatty acid of very high saponification value and acid number showing that the unsaponifiable material formed by hydrogenation had been eliminated.

\* U. S. Patent No. 1,209,512, December 19, 1916.

Proceeding along similar lines the fatty acids of cottonseed, fish, whale and other vegetable or animal oils may be treated to form high-grade fatty acids suitable for the manufacture of first-class toilet soaps.

According to a method of the **Reuter Process Co.,\*** in the production of fatty acids by boiling glycerides with organic catalytic hydrolyzers, the hydrolysis is effected in a number of stages, in each of which stages a fraction of the total amount of hydrolyzer is added, the mixture being allowed to settle after each boil and a dark-colored intermediate layer of impurities is removed, after which more hydrolyzer is added and boiling resumed. Air is excluded from the saponification tank. The fatty acids thus produced, and soap and candles made therefrom, after aging for ten days after making, do not darken substantially in color on exposure to air and light. Glycerides used in this process may be the following, separately or collectively: Beef and mutton tallow; horse, hog, and butter fats and their greases; whale, menhaden, fish, cocoanut, peanut, linseed, cottonseed, palm, palm-kernel, and soya-bean oils; and the hydrogenation products of corn oil, linseed and cottonseed oils, fish oil, etc.

**Schauth †** calls attention to the advantages of the ordinary Varrentrapp reaction and notes that while the hydrogenation process produces fats which can be employed in lathering soaps only by the addition of other fats and fatty acids that the product obtained by the Varrentrapp reaction is more readily available in soap making. He also suggests that the hydrogen formed during the Varrentrapp reaction be used for hydrogenation purposes.

Highly hardened oil such as a thoroughly hardened cottonseed oil is used by **Ellis ‡** to produce a flattening effect in paint compositions so that the surface will dry to a matt finish.

Hydrogenated castor oil is used by **Cordes §** as an insulating or impregnating material for telephone condensers.

In manufacturing these condensers, long strips of paper are laid on strips of tin-foil, the two strips are then rolled up, and the coils thus formed are pressed into a rectangular shape and dried either with or without the use of a vacuum. The coils of paper and tin-foil are then mounted in frames, the frames with the coils thereon are placed in a vacuum-impregnating receptacle containing the hydrogenated castor oil and the coils are heated, for which purpose the receptacle has a heating jacket which receives steam at a pressure of about two atmospheres. The molten fat is in this way caused to penetrate between the paper and the tin-foil and the moisture is expelled by the heat in the form of

\* British Patent No. 9,394, June 26, 1915.

† Chemical Eng. and Mfg., Vol. XXIV, 1916, 204.

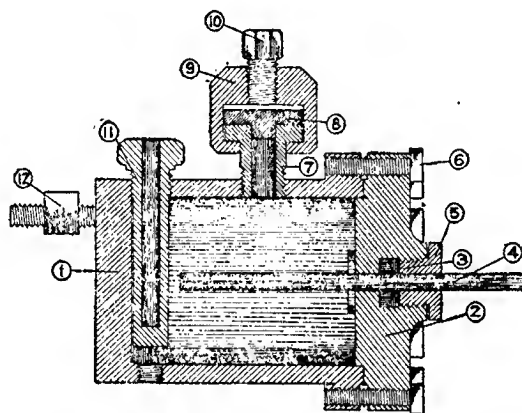
‡ U. S. Patent No. 1,173,183, February 29, 1916.

§ U. S. Patent No. 1,241,926, October 2, 1917. See also Nos. 1,276,507, 1,276,508 and 1,276,509 issued August 20, 1918 to Ellis.



bubbles. The vessel is subsequently sealed hermetically, and the extraction of moisture continues until the last trace has been removed from the paper, this part of the process occupying from two to four hours. After the moisture has been thoroughly extracted, cold water is introduced into the jacket. Owing to the high dielectric properties of the impregnating material, it is possible to obtain the same effects with condensers, which are only half as large as those necessary with the use of paraffin.

In a study of corn oil with reference to its use as a substitute for olive oil in various unctuous preparations such as liniments, ointments, cerates, plasters and oleates, **Lackey** and **Sayre** investigated the hydrogenation of corn oil.\* Apparatus was used as shown in Fig. 54b.



Cross Section of Autoclave

FIG. 54b.

Comparative tests on the hydrogenation of corn oil and similar oils of about the same iodine value were made. Nickel oxide was used as the source of catalytic material. A temperature of about 200° C. was used with hydrogen at 50 lb. pressure. In six hours time a product was obtained from corn oil melting at about 36° C. The following table shows comparative results with cottonseed and corn oil:

COTTONSEED OIL		CORN OIL	
Time, Hours.	Melting-point, ° C	Time, Hours.	Melting-point, ° C
6	35	5½	31
10	39	7	34
7	35	7	33
3	29	3½	23

\* J. Am. Pharm. Assn., Vol. VI, April, 1917, 349.

It is noted by Lackey and Sayre that the presence of the small amount of nickel remaining in the fat after filtration from the catalyzer is not of sufficient moment to interfere with, or be objectionable in, making most of the unctuous preparations referred to. One merit of the hydrogenated product is its keeping qualities. Lackey and Sayre have kept samples of hydrogenated corn oil for over a year which have not shown the least indication of rancidity.

Hydrogenated corn oil when well hardened possesses the property of expanding on passing from the molten to the solid state and when run into barrels and allowed to solidify this form of hard fat has been observed to break the hoops of the barrels during the period of expansion. In this respect corn oil resembles, in a lesser degree, highly hardened Chinese wood oil. (See page 361).

Fox \* notes that practically all the semi-drying oils (except Chinese wood oil) are capable of use for lubricants, as they can be hydrogenised and converted into non-drying oils. He prepared a lubricating oil from hydrogenised soya bean oil mixed with 14 per cent of mineral oil. A lubricating grease, similarly made, was used in the gearbox of a motor car for nearly a year.

Ellis † incorporated hydrogenated oil and pulverulent material. The product may take either of two forms. (1) a solid cake or semi-solid coherent mass and (2) a comminuted or pulverulent product. The solid cake may be used for a variety of purposes such as buffing and grinding, lubricating, polishing and the like. A lubricating powder may be made, for example, from equal weights of hydrogenated oil and graphite. A buffing or grinding composition may be produced from hydrogenated oil and an abrasive powder such as crocus or carborundum and emery. A tailor's chalk may be made by melting hydrogenated cottonseed oil of m.p. 60° C. with a quantity of talc. Products in the powdered form containing hydrogenated oil and carbohydrates may be used for edible purposes.

Referring to the imports at Pacific ports of dog-fish, halibut, salmon, sardine, shark, tuna fish, candle fish, walrus, whale, seal and porpoise oils, Sadtler ‡ states such oils have an added value since the general application of the hydrogenation process as they can be changed into hardened fats valuable to the soap and glycerine manufacturer.

\* J. S. C. I. 1918, 304R.

† U. S. Patents Nos. 1,276,507, 1,276,508 and 1,276,509, August 20, 1918.

‡ Chem. Met. Eng. 1918, 558.

## CHAPTER XVII

### HYDROGENATION PRACTICE

Whether or not the plant is to treat animal or vegetable oils, or fish oil, the following general procedure may be laid down for guidance in the equipment and operation of a hydrogenating works.

The starting point is, perhaps, the preparation of catalyzer. Of course the procedure employed for its preparation depends on the type of catalyzer selected. Suppose nickel be chosen as the active material, to be used on a suitable carrier or supporting base. To this end a solution of a nickel salt, such as the nitrate or sulfate, is mixed in vats with the support, in the presence of a precipitant, or the latter is subsequently added, and the material is well agitated. Soluble salts should then be removed by washing and the material dried. These operations may take place in a filter press supplied with air under pressure. The caked product should be ground in a ball or pebble mill until resolved into a fine powder.

The catalyzer is now ready for reduction, which should be performed with extreme care as the entire oil-hardening process depends on the efficiency of the catalyzer. A simple and efficient type of catalyzer-reducing device is represented by Fig. 55. *A* is a brick structure which contains the reducing drum *B*. The latter is rotated by means of the sprocket *C*. *E<sup>1</sup>E<sup>2</sup>* are stuffing boxes which admit of rotating the drum without disturbing the gas inlet and outlet. The catalyzer is admitted and withdrawn through the gate *G*. The drum is filled about two-fifths full of the catalyzer and hydrogen passed in. When tests for oxygen show that all the air has been expelled the drum is heated to a temperature not exceeding 360° C. During reduction the hydrogen is passed through at a considerable rate in order to remove the steam formed, thus reducing the partial pressure of the latter and facilitating the reduction of the nickel oxide or hydrate. The gases issuing from the exit side of the drum may pass through a water seal and after purification may be returned to the gas holders to be used again. When the issuing gases are found to contain no steam the reduction is complete, the heating is discontinued and the catalyzer allowed to cool in a current of hydrogen.

After cooling the catalyzer, the hopper shown in Fig. 55 is coupled to the flange of the gate *G*. The bottom of the hopper dips below the surface of oil contained in a receptacle beneath. Hydrogen is passed in at the valve *J* and the air is thereby expelled from the hopper. The valve of the reducing drum is now opened and the catalyzer allowed to fall into the oil with which it should be thoroughly mixed. Thus the catalyzer is effectively sealed from the air.

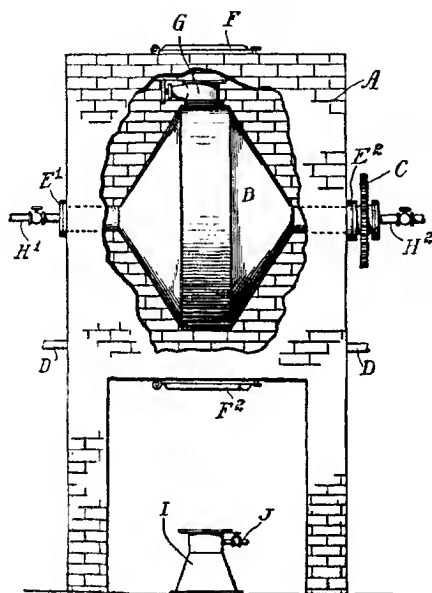


FIG. 55.

This method of abstracting catalyzer from the reducing drum prevents oxidation of the nickel which occurs to a greater or less extent when the catalyzer is withdrawn in contact with the air.

The catalyzer in oil may then be transferred to a large agitating tank in which oil is added in sufficient quantity to make the mixture contain the correct percentage of catalyzer. The contents are thoroughly agitated and transferred to the hydrogenator where the actual hydrogenation takes place.

Tall iron tanks may be used for this purpose, one type of which is shown in Fig. 56. The air in the hydrogenator is displaced by means of hydrogen and the mixture of catalyzer and oil pumped from the

agitator *A* into the hydrogenator *C*. The contents of the hydrogenator are heated to a temperature of 175° to 190° C. by means of superheated steam or hot oil coils, the latter being preferable owing to the danger of leakages of steam into the chamber. The temperature of the contents of the hydrogenator should be registered by means of a reliable thermometer, preferably a recording pyrometer.

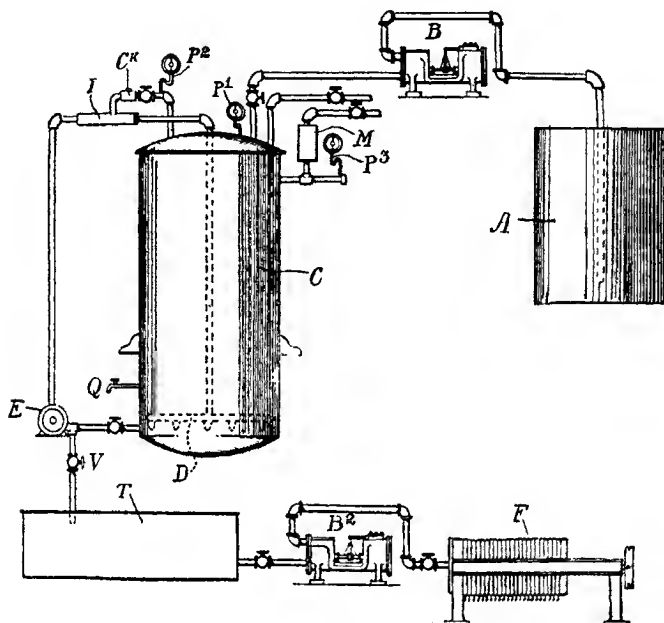


FIG. 56.

The oil and catalyzer in the hydrogenator are circulated by means of the rotary pump *E*, which takes the liquid from the bottom of the hydrogenator and pumps it through the inductor *I* where hydrogen drawn from the gas space at the top of the hydrogenator is mixed with the oil. *C<sup>K</sup>* is a check valve to prevent oil from entering the tank through the suction tube in the event of the inductor suction nozzle becoming flooded. The mixture of oil, catalyzer and hydrogen is ejected through the distributor *D* at the bottom of the hydrogenator.

The hydrogen inlet is provided with a safety device *M* and a pressure gauge *P<sub>3</sub>*.

The pressure maintained in the hydrogenator is variable according to the oil under treatment and may range from atmospheric or less up to about 25 pounds.\* The difference in the readings of the pressure gauges  $P_1P_2$  registers the suction of hydrogen at the suction nozzle of the inductor. Samples of oil may be withdrawn from time to time from the outlet  $Q$ . When the sample indicates that the oil has the required hardness the hydrogenator is emptied through the outlet  $V$  and the contents are run into large tanks which are heated by means of steam coils. From these tanks the mixture of oil and catalyzer is pumped into filter presses where the catalyzer is removed. The oil is finally run into cooling tanks where it solidifies to a hard fat ready to be made into lard compound, soap or other product.

The transformation to olein of the glycerides of linoleic and linolenic acids or other highly unsaturated acids usually does not result in any marked change in the titer. As these bodies sometimes are, to a considerable extent, transformed into olein before olein becomes stearin, hydrogen will be absorbed by the oil without hardening, to a degree dependant on the proportion of these highly unsaturated bodies present. Often an hour or more is needed to bring an oil to the "olein stage," after which hardening will progress rapidly.

Of course, the method given above is capable of many modifications, as oils of different character require different treatment and in consequence oftentimes call for equipment which varies considerably from that given by way of illustration. Catalyzers vary a good deal in their properties, and conditions which are suitable for nickel in some of its forms will not answer for palladium. A much lower temperature usually suffices when using the latter metal as a catalytic substance.†

A simple type of converter now extensively used is shown in Fig. 56a. It consists of a closed tank equipped with a steam coil and stirrer. The vessel is charged with oil and catalyzer and the charge is heated to the requisite temperature when hydrogen is introduced by the small pipes in the bottom of the apparatus. The oil is stirred vigorously during the operation. Heat is developed in hydrogenating fatty oils

\* One of the difficulties met with in the handling of hydrogen has been the loss by leakage of the gas. Under pressure and at a temperature of 150° or 200° C., hydrogen is surprisingly penetrating. Autoclaves with welded seams are desirable for high-pressure and high-temperature work. Moving parts should be avoided as far as possible.

† Reference is made to the chapter on catalyzers which gives much detailed information on the subject. Attention is, however, called to the existence of several patents covering certain forms of catalytic preparations.

and when a considerable quantity of oil is being hardened, the heat of reaction may be not only sufficient to maintain the batch at the reacting temperature but may even cause the temperature to rise too high, so that cooling is needed. This is especially noticeable with

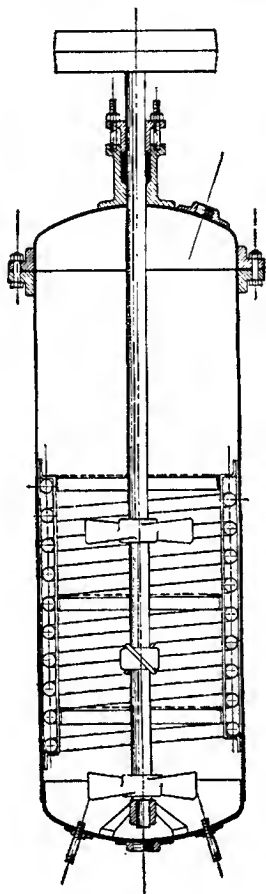


FIG. 56a.

freshly-prepared catalyzer. Sometimes preliminary heating by steam to  $100^{\circ}$  to  $120^{\circ}$  C. suffices to start the reaction and the temperature rises rapidly. At  $170^{\circ}$  to  $180^{\circ}$  C. water may be passed through the coil to prevent overheating.

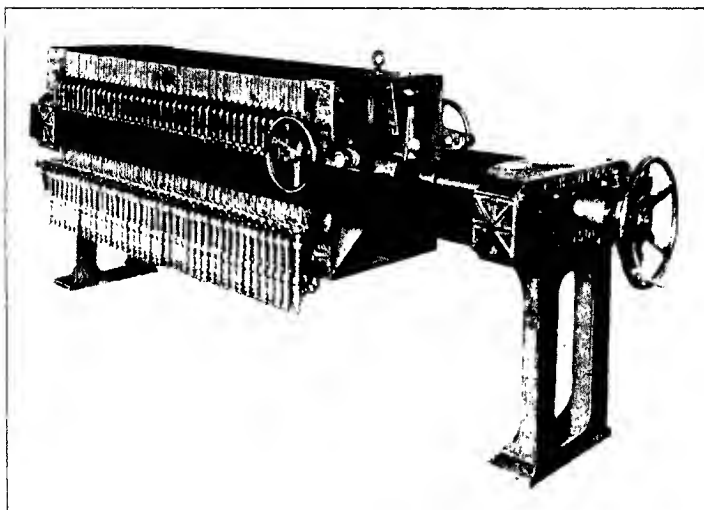


FIG. 56b.—Shriver Filter Press for Filtering Hardened Oil.

The filtration of oil to remove finely-divided nickel, especially when in a colloidal or partially colloidal condition, is aided by the addition of fuller's earth, silicex or some similar bulking material.\*

\* U. S. Patent to Ellis, No. 1,158,664, Nov. 2, 1915.



## CHAPTER XVIII

### THE HYDROGENATION OF PETROLEUM

THE hydrogenation of the unsaturated constituents of petroleum has proved to be a fascinating subject of research by chemists and the literature on this topic has been greatly augmented of late.\* See pages 11 and 21 for earlier data.

The results of experiments by Winkler † on the problem of motor gasoline are of interest. Winkler observes that California petroleum is one of the large sources for gasoline, and yet that probably 80 per cent of it is too thick for any explosive mixture and "a sootless burn" in the cylinder. To depolymerize the heavy hydrocarbon oils down to their simplexes somewhat analogous to the depolymerization of synthetic rubber back to isoprene—the following experiments were carried out:

First, by way of explanation, "cracking" of these oils by mere superheating, he states, has proved totally unprofitable in California factories; and so have all kinds of pyrogenic experiments in his laboratory (i.e., passing the vapors with hydrogen through hot tubes containing various metals). The results have not shown promise as the products go largely into the sludge in refining, and have penetrating odors. The oils show great tendency to thicken when heated, especially in contact with various substances, as air, alkali, concentrated sulphuric acid, and various salts, as aluminum chloride. The best results, he notes, are obtained by distillation in an atmosphere of hydrogen. In addition to the unsaturated cyclic bodies, and the sulphur and nitrogenous compounds, these oils contain benzol ring bodies with side chains, as the mesitylenes, forming the turpentine substitutes. Asphalt occurs therein as a colloid,‡ and is eliminated at the start by fractional steam distillation. Winkler's experiments are as follows:

1. *Effect of Corona.* A glass tube  $2\frac{1}{4}$  in. diameter by  $3\frac{1}{2}$  ft. long, wrapped with wire gauze, with a  $\frac{1}{4}$ -in. copper rod suspended co-axially through its centre, was used as a hot vapor chamber, while at the same time the inside rod and outside gauze were kept at a potential of from 25,000 to 30,000 volts by dynamo and high potential transformer. When the room was darkened, a continuous bright bluish glow was evident throughout the tube, i.e., a corona. Through this glow (air removed) various California heavy distillates were distilled repeatedly, with a large excess of hydrogen (dry and moist), the object of the corona being to ionize the hydrogen. (The dielec-

\* Cf. Moore and Egloff on "Fats and Fatty Acids from Petroleum," *Met. and Chem. Eng.*, 1918, 309. See also Bureau of Mines, Bulletin 149, Bibliography of Petroleum, by Burroughs.

† J. Franklin Inst., 178, 1914, 97.

‡ Z. Ang. Ch., 1913, 609.

tric constants of hydrogen and hydrocarbon vapors and air were found to be not very different.) Practically no change could be detected in the oils after repeated slow distillations through the above chamber.

2. *Effect of Arc.* The Birkeland-Eyde process was applied to these oils in an atmosphere of hydrogen. The oils, both liquid and gaseous, were passed through with increasing speed, to shorten the time in the arc. The carbons were hollow, and hydrogen was passed inward through both. They were kept cool by a water jacket. The results were variable, but in every case the oils were reduced to non-condensable gases and a cloud of fine carbon.

3. *Effect of Steam and Aluminum under Pressure.* Very fine aluminum dust was mixed with various heavy California oils to a "suspension," and these mixtures subjected to a pressure of 110 lb. per square inch with steam in a heavy, specially constructed retort. They were also agitated, and at the same time heated to various temperatures (indicated by thermometer) up to their cracking points. The purpose of the aluminum and steam was to generate nascent hydrogen within the oil. A variety of attempts indicated no success. The aluminum was not amalgamated.

4. *Effect of Reduced Nickel Oxide and Hydrogen on the Aerated Oil.* According to Charitschkoff, better results at "cracking" Russian petroleum were obtained by first oxidizing the oil.\* Heavy California oils were heated and aerated (by drawing air through them) for two or three days, to oxidize them and to generate petroleum acids (the purpose of this oxidation also being to introduce carboxyl groups, with the possibility of splitting out water with the hydrogen afterwards, and leaving the rest of the broken molecule to unite with the excess hydrogen). The aerated oils were subjected to the action of reduced nickel oxide and hydrogen (said to be least sensitive to sulphur compounds, † but without success. Iodine was substituted for the nickel oxide with no better results.

5. *Effect of Rhodium Black and Hydrogen.* First, active platinum black, made according to the Loew process, ‡ has been shown to be a good catalyst to hydrogenate pure benzol and pure benzene. It is, however, poisoned by sulphur bodies.§ California oils contain sulphur, and do not hydrogenate under these conditions.

Bredig has shown that rhodium metal acts as a catalyst to break down formic and acetic acids to hydrogen and carbon dioxide, etc., and that sulphur bodies are favorable to its activity.|| Rhodium black was made (by the Loew process), and tried out on California oils under parallel conditions, but failed to hydrogenate in the least.

Snelling¶ is able to produce a high-grade petroleum, yielding substantial proportions of gasoline and kerosene fractions, from low-grade crude oils and petroleum products such as gas oil, by heating them to a temperature such that the vapors evolved will produce an added pressure of at least 400 lb. per square inch, the quantity of liquid in the container being such

\* "Petroleum," 1913, 748.

† Z. angew. Chem., 1913, 561-606.

‡ Ber. 23, 289.

§ Ibid., 45, 1471.

|| Oest. Ch. Ztg., No. 14, 1911, 266.

¶ British Patent No. 18,419, Aug. 7, 1914; Chem. Abs., 1916, 388. Cf. O. P. & Drug Reporter, Apr. 5, 1915, 33. Gasoline from Synthetic Crude Oil, by Snelling.

that it occupies not less than one-tenth and not more than seven-tenths of the total capacity of the container.

The operation may be effected in the presence of a catalyst such as colloidal graphite, colloidal carbon (formed by producing an arc between carbon points immersed in the oil), or nickel or other metal in the colloidal form, or in the presence of gases and vapors such as hydrogen, natural gas, ethylene, oil gas, water-gas, or steam. Temperatures in excess of  $380^{\circ}$  and below  $600^{\circ}$ , preferably between  $400$  and  $500^{\circ}$ , are employed. Pressures between 600 and 800 lb. per square inch are preferred, though a pressure of 2400 lb. per square inch may be employed. According to one method of treatment, the oil is heated until the pressure reaches 800 lb. per square inch, and is then allowed to cool. The permanent gases are allowed to escape, and may be used for heating or for making propane or butane. The oil is fractionated up to  $150^{\circ}$ , and the residue is subjected to a further treatment.

According to Oildom,\* petroleum and other heavy hydrocarbons are cracked by heating them in a cracking-still, together with a catalyst, such as finely-divided nickel, and hydrogen or purified water-gas, with violent agitation.

The vapors may be passed through a chamber, containing a finely-divided catalyst, such as asbestos, coated with nickel, on their way to the condenser.

The heavy hydrocarbon is first purified from asphalt, sulphur, and other catalyst poisons, and is passed from the store-tank, together with hydrogen from a reservoir along a pipe, where it mixes with nickel from a shot-flask device, entering the still through a rose. The still is fitted with an agitator. The distillation is effected at about  $300^{\circ}$  C. and under a pressure of 5-1000 lb. per square inch regulated by a weighted valve. The gases which escape from the condenser are burnt under the still, or, if rich in hydrogen, are readmitted to the still. The nickel is regenerated when necessary by washing it with benzol, calcining to oxide, converting into citrate or formate, and reducing with hydrogen at  $320$  to  $350^{\circ}$  C. Instead of providing the cracking-still with a large exposed upper surface, a reflux condenser may be used.

**Planes Limited** † produce saturated lighter hydrocarbons from heavier oil according to the following method:

The heavier oil together with nickel catalyzer and hydrogen or hydrogen-containing gas are run into a tall cracking still, the latter being provided with a stirring device. As the temperature rises pressure is developed to the desired point when it is relieved by a weighted valve into an expansion chamber. This chamber is fitted with shelves on which are placed catalytic material. The vapors from the still pass through this chamber together with water gas and are saturated. They are then condensed. Oil, catalyzer and hydrogen are continuously passed into the still until the residues are too heavy to be further cracked, when they are removed and the catalyzer recovered. The waste gases may be returned to the still provided they are still rich in hydrogen.

\* Dec., 1914, p. 19.

† British Patent No. 5,245, Apr. 1, 1914.

Mineral oils and residues are treated for the production of lower boiling hydrocarbons by **White** \* as follows:

The oil or residue, with or without preliminary distillation, is distributed in a liquid state, and without the addition of steam, on to the surface of quicklime which has been heated to 500° to 600° C. in a retort or chamber. The vapors of lower boiling-point thus produced may be drawn off by suction and fractionated. Crude paraffin oil thus treated yields 20 to 25 per cent of hydrocarbons with flash-point and boiling-point similar to those of gasoline. The lime may be regenerated by burning off the deposit of carbon.†

By a process for eliminating sulphur from oil, advanced by **Evans**,‡ the oil is vaporized, mixed with 5 to 10 per cent of hydrogen, or with a gas containing hydrogen, and passed over a heated catalytic or contact substance such as nickel deposited on fire clay. Hydrogen sulphide is formed, and may be removed. If the oil cannot be distilled, it may be heated in contact with the catalyst while hydrogen is passed through or over it.

**Porges** and **Stransky**§ increase the volatility of hydrocarbons in the following way: the vapors of the latter, mixed with steam, at a temperature below 600°, are brought into contact with metallic oxides such as the oxides of lead and nickel which function as catalyzers. A portion of the hydrocarbon is converted into carbon dioxide by reduction of the metallic oxide which is regenerated by means of air or oxygen.

**Chichibabin** || suggests that the catalytic influence of metallic oxides and certain salts on the formation of sulphur and nitrogen containing substances and on the condensation of lower to higher hydrocarbons observed by **Sabatier** and by **Ipatiev** lends support to the hypothesis of the mineral origin of naphtha, there being an abundance of such catalyzers in the bowels of the earth. As to the optical activity of natural naphtha, it speaks neither for nor against this hypothesis, until its exact causes are learned. To assume that this activity is due to living forces is for the present unwarranted.

**Heyl** and **Baker** ¶ in their process of producing motor spirit, dissolve hydrogen in liquid fuels such as gasoline, benzine, or alcohol by spraying the liquid into the gas within a chamber supplied with a safety valve. The solution may be passed over cold or heated aluminum, nickel or other catalyst in a tube to aid the retention of the gas. In a smaller apparatus, twin opposing nozzles are used.

In the manufacture of condensation products from unsaturated hydrocarbons **Schering** \*\* uses anhydrous inorganic chlorides, as catalyzers. These are allowed to act upon mixtures of paraffin hydrocarbons with hydrocarbons poorer in hydrogen which contain at least two double bonds. The reaction products of a previous run can be employed also as catalyzers.

\* British Patent No. 5,434, Mar. 3, 1914.

† J. S. C. I., 1915, 651.

‡ British Patent No. 22,147, Nov. 6, 1914; J. S. C. I., 1915, 1241.

§ Italian Patent No. 142,453, May 30, 1914; Chem. Abs., 1915, 2814.

|| J. Russ. Phys. Chem. Soc., 1915, 714; Chem. Abs., 1915, 2489.

¶ British Patent No. 11,756, May 20, 1913.

\*\* German Patent No. 278,486, May 24, 1913.

**Franke** \* claims that motor spirit is obtained from peat tar by distilling up to 320° and redistilling the distillate, preferably after it has been purified, up to 250°. The second distillation may be stopped at 170°, and the residue then heated up to 300° under pressure of 25 atmospheres in order to crack it.

The cracking is accelerated by the addition of a catalytic agent capable of recombining with the oil, the hydrogen which is evolved in the cracking; pyrophoric metals, such as iron, nickel, chromium and platinum are suitable for this purpose. The product of the first distillation is purified by treatment with oxidizing or condensing agents, preceded by the usual acid and alkali treatment. The oil is first treated with sulphuric acid, then washed and treated with a solution of caustic soda and again washed. Finally air is blown through the heated oil until it clarifies. Instead of oxidizing the residual phenolic compounds by treatment with air, manganese dioxide and sulphuric acid, or peroxides, persulphates, or chlorates, may be used, or condensing agents such as zinc or aluminum may be employed. The resinified phenolic compounds are removed by filtration before the second distillation.

**Holcgreber** † obtains benzene by passing the vapors of petroleum or its distillates, together with hydrogen through a tube containing catalytic materials, and heated to 180 to 300°. Acetylene is said to be first formed and then become polymerized to benzene. Suitable catalysts are iron, copper, zinc, aluminum, nickel, cobalt, silver and platinum or mixtures of these metals.

**Ellis and Wells** ‡ describe the results of experiments with several forms of tubular cracking apparatus and the hydrogenation of some of the products obtained.

Using kerosene of 42° B. (sp.gr. 0.814) yields of gasoline (boiling-point up to 150° C.) of 18 to 20 per cent were obtained at 450° to 600° C. By distilling off the gasoline and retreating the residue, and also scrubbing the gaseous reaction products with oil, yields of 40 to 45 per cent of gasoline were obtained. The gasoline was denser than normal gasoline of the same boiling-point, had a higher refractive index and was unsaturated; the iodine value of the distillation fractions was higher the lower the boiling-point, a fraction boiling below 70° C., for example, having an iodine value of about 300. On standing for a long time the gasoline became darker in color, and when subsequently distilled, a violent reaction occurred at about 160° C., resulting in the production of a dark brown viscous oil. A similar reaction occurred at about 110° C. on distilling under diminished pressure (6 to 10 mm.). The viscous polymerized product reacted violently with sulphur and with sulphur chlorides, a viscous oily mass being produced. Hydrogenation improved the odor of the gasoline, changed the color from light straw-color to water-white, and destroyed the tendency to polymerize.

\* British Patent No. 13,361, June 7, 1913.

† British Patent No. 17,272, July 28, 1913.

‡ J. Ind. Eng. Chem., 1915, 1029; J. S. C. I., 1916, 102.

**Tinkler and Challenger** \* state that the objectionable smell of cracked oils is removed by hydrogenation.

**Danckwardt** † produces gasoline from crude oil by introducing a spray of molten lead, alloy or fused sodium nitrate, caustic soda or other liquid, insoluble in the oil and not distilling at the temperature employed, into the vapor space of the retort used and thence into the liquid in the retort. The added material is withdrawn from the retort and returned again to the retort after passing it through a heater. Vapor from the retort is continuously drawn off and condensed.

**Testelin and Renard** ‡ have proposed an apparatus for making volatile hydrocarbons from petroleum in the use of which the oil is passed under high pressure over refractory material such as clay which is maintained at a red heat. Steam is introduced with the oil.

**Moeller and Woltereck** § crack heavy oils by mixing their vapors with highly superheated steam at substantially atmospheric pressure and passing the mixture over coke at a dull red heat ( $600^{\circ}$  to  $800^{\circ}$ ). The sulphur present in the oil is at the same time converted into hydrogen sulphide and is thus removed from the oil. The steam is superheated to  $700^{\circ}$  to  $800^{\circ}$  in an apparatus which allows the steam to expand while it is being heated.

A process for improving the quality of hydrocarbon oils is described by the **Badische Company** ||. The oils are decolorized and deodorized by treatment in the fluid condition with hydrogen, at not above  $200^{\circ}$  C., at atmospheric or increased pressure, and in the presence of a catalyst, such as nickel, iron, cobalt or copper, or mixtures of these.

The **Badische Company** ¶ produces hydrocarbons, which are easily liquefiable, and oxygen derivatives of hydrocarbons by passing carbon monoxide and hydrogen mixed or not with other gases, in the proportions of at least two-thirds of a volume of the former to one volume of the latter, over a heated catalyst under a high pressure exceeding that of five atmospheres. In examples, the preparation of hydrocarbons boiling from  $20^{\circ}$  up to  $250^{\circ}$ , of olefines, paraffins, and benzine hydrocarbons, of alcohol, ketones, such as acetone, aldehydes such as formaldehyde, acids such as acetic and its homologues and other products are described. In some cases, a basic compound is added to the catalyst and mixtures of two or more catalysts may be employed.

**Brooks, Bacon, Padgett and Humphrey**\*\* state that the effect of pressure in diminishing the per cent of olefines in the gasoline obtained is a note-

\* Chemistry of Petroleum and its Substitutes, p. 194. (See also pages 243 to 254.)

† U. S. Patent No. 1,141,529, June 1, 1915; Chem. Abs., 1915, 1994.

‡ U. S. Patent No. 1,138,260, May 4, 1915; Chem. Abs., 1915, 1689.

§ British Patent No. 16,611, July 19, 1913; Chem. Abs., 1915, 148.

|| French Patent No. 472,776, May 28, 1914; J. S. C. I., 1915, 540.

¶ British Patent No. 20,488, Sept. 10, 1914.

\*\* J. Ind. and Eng. Chem., 1915, 180 and 412.

worthy feature of their work. The same effect is very strikingly shown in the interesting results of Whitaker and Rittman on the effect of pressure in the yield of illuminants in oil gas. At 900° C., Whitaker and Rittman obtained from a given quantity of oil 122 liters of illuminants at 0.75 lb. pressure, 50 liters at atmospheric pressure and 15.5 liters at 45 lb. (absolute) pressure. They were also able to show that at temperatures of 750° to 800° C. the addition of hydrogen to the gas mixture has the effect of partially hydrogenating the olefines and that this reaction takes place more readily as the pressure on the system is increased. Ipatiew\* has made the interesting observation that, in the distillation of petroleum under pressure, at the higher pressure the evolved gases become continually poorer in hydrogen in spite of the higher temperatures required to maintain the higher pressures. The pressures employed by Ipatiew were 120 to 340 atmospheres.

The liberation of hydrogen from petroleum hydrocarbons at various temperatures has been studied by Engler† and his students. They obtained no hydrogen below 470° at atmospheric pressure from kerosene fractions boiling below 280° C. The liberation of hydrogen from different hydrocarbons at a given temperature depends somewhat on their constitution. Thus, benzol yields appreciable quantities of hydrogen only at temperatures above 500° C.

The work of Brooks, Bacon, Padgett and Humphrey indicates that if hydrogenation of the liquid olefines takes place during distillation under pressure, it occurs simultaneously with their initial formation. A sample of cracked naphtha, having an iodine number of 55.0 was heated to 196° C. with hydrogen for thirty hours under 3000 lb. pressure per square inch. The iodine number and refining loss with sulphuric acid were practically unaffected, the iodine number of the final product being 52.9. Results closely parallel to this were obtained by Rhodes, working with liquid fatty oils. The apparatus employed was a steel bomb connected with a solenoid stirrer constructed as described by Stueker and Enduli.‡ Uebelohde and Woronin§ showed that in the presence of nickel, hydrogen was split off from a Baku crude oil at as low a temperature as 180° C. The results of Zelinski|| with dehydrogenation at temperatures above 300° C. in the presence of platinum is to be expected. Ostromisslenski and Bujanadse¶ showed that in the presence of nickel a Russian crude oil gave only coke, 40 per cent, and gas at temperatures between 660° to 700° C., no tar or liquid being obtained at all. Furthermore, the gas contained 72 to 75 per cent of hydrogen and the remainder consisted of saturated hydrocarbons. These facts are quite significant in view of the proposed cracking processes of Vernon Boys, Lamplough and others, who introduce nickel into the cracking zone. A series of experiments were made by Brooks, Bacon Padgett and Humphrey at atmospheric pressure and at temperatures of 500° to 550° C., employing various catalytic substances. Kerosene and solar oil vapors passed through an iron tube containing

\* Ber., 1904, 2969.

† Engler and Hofer, *Das Erdöl*, 1, 574.

‡ *Zeitschr. f. Elektroch.*, 1913, 570.

§ *Petroleum*, Berlin, 1911, 7.

|| Ber., 1912, 45, 3678.

¶ *J. Russ. phys.-chem. Ges.*, 1910, 195.

burned clay, carbon, coarse and finely-divided iron, coarse and finely-divided copper, heated to the above-named temperature, yielded gasoline fractions, which showed an olefine content of approximately 25 to 30 per cent. When nickel was employed the per cent of olefines in the gasoline product was 48 per cent.

**Humphreys**\* obtains low boiling hydrocarbons from liquid paraffin hydrocarbons of petroleum which boil at 260° or higher by distilling a portion of the liquid under four atmospheres or higher pressure at a temperature of 340° to 455° in a still containing steel, brass or copper plates immersed in the liquid. The plates are stated to have a catalytic action in forming lighter hydrocarbons and about 65 to 70 per cent of the liquid treated is distilled off and condensed.

A process and apparatus for converting heavy into light hydrocarbons is described by **Porges, Stransky and Strache**.†

A mixture of the vaporized oil and steam is passed over a catalyst (iron oxide or oxide of another metal capable of forming several oxides), which is heated to 500 to 600° C., and light products are formed. When the hydrocarbons begin to diminish the catalyst is regenerated by heating it in a current of air or oxygen.

The **Continental Caoutchouc and Gutta Percha Co.**‡ heat a mineral oil fraction of high boiling-point with a catalyst such as aluminum chloride, with or without mercuric, ferric, vanadium, or other chloride, or with aluminum in a stream of dry hydrochloric acid gas, or the oil is atomized and exposed to ultra violet rays or the silent electric discharge in presence of a catalyst. The process is continuous. Gaseous products are obtained by heating to a higher temperature, and longer, in closed vessels.§

**Brooks**|| obtained from 3 to 20 per cent of gasoline, boiling below 150° C., by cracking Texas solar oil (sp. gr. 0.8862) alone and in the presence of various contact substances, at temperatures between 400° and 600° C., at atmospheric pressure; the gasoline was highly unsaturated, the loss by treatment with concentrated sulphuric acid averaging about 28 per cent. Various proposed methods of hydrogenation are also considered; the oil-steam iron process for hydrogenating olefines and preventing deposition of carbon is stated to be inadequate.

The disagreeable odor of highly cracked gasoline was removed by treatment (desulphurization) with alkaline plumbite, copper oxide, or metallic sodium. In experiments on the distillation of heavy petroleum oils, mainly Oklahoma reduced oil, 30° B. (sp.gr. 0.875) under pressures up to 450 lb. per square inch, the yield of

\* U. S. Patent No. 1,122,003, Dec. 22, 1915; Chem. Abs., 1915, 374.

† British Patent No. 11,420, May 8, 1914. See also U. S. Patent 1,205,578, Nov. 21, 1916, to Strache and Porges.

‡ French Patent No. 469,948, March 21, 1914.

§ Chem. Abs., 1915, 19.

|| J. Franklin Inst., 1915, 180, 653; J. S. C. I., 1916, 102.



gasoline increased with the pressure, up to about 32 per cent at 250 lb., and then declined; the olefine content of the gasoline decreased as the pressure increased up to 200 lb. and then remained constant, this result being ascribed to polymerization rather than hydrogenation. As regards processes in which oil is cracked while in the form of vapor, it is pointed out that heavy oil can only be completely vaporized at very low pressures. Gasoline obtained by cracking the vapor of Oklahoma reduced oil under a pressure of 100 lb. per square inch, consisted chiefly of normal paraffin hydrocarbons but contained about 8 per cent of benzene, toluene, and *m*-xylene. The formation of aromatic hydrocarbons from petroleum oils by this means is regarded as due to the splitting or cracking of high-boiling complex hydrocarbons containing the phenyl radicle (not to the dehydrogenation of naphthalenes, formation of acetylene, and condensation of the latter to benzene, etc.), and evidence is adduced in support of this hypothesis.

The *Scientific American*,\* observes that an English company is securing a very large yield of gasoline from petroleum by catalytic hydrogenation. The method is practically the same as that recently applied in the conversion of liquid fats to a solid form or to solid fatty acids with a higher value. A tall still with a conical bottom receives a steady feed of petroleum and hydrogen gas under pressure. This mixture enters at the bottom and passes over finely-divided nickel which catalytically brings about a reaction between the hydrogen and oil. Gasoline is formed which passes off as a vapor at the temperature of the still, while the heavier hydrocarbons formed fall back into the catalyst and react with hydrogen. Finally a tarry residue must be removed and the nickel regenerated. The issuing gases pass into a cooling chamber where the gasoline is condensed. The hydrogen unused up to that point is forced back and passed through the still once more.

By a cracking process of **Valpy** and **Lucas**,† steam is superheated to a temperature slightly below the cracking-point and is sprayed into the oil in a still. The mixture of oil, vapor and steam is passed through heated catalyzing tubes of nickel, which may be packed with catalyzing material, and thence to a coil in the oil still where the heat of the cracked vapor is utilized for heating the oil. The catalyzing tubes may be heated electrically, or by an oil burner.‡

A modification of this method of cracking oil of **Valpy** and **Lucas**,§ consists in removing oil vapor from a still by means of steam or an inert gas under pressure and the mixture is brought into contact with a heated catalyst, such as nickel or one of its alloys, or nickel suboxide or oxide, and, the pressure of the mixture after leaving the catalyzing chamber is reduced suddenly. The light oils produced are condensed.||

A catalyst for cracking petroleum oils described by **Lucas** ¶ is prepared by heating a mixture of oxides and oxalates of iron and nickel, chromium

\* May 23, 1914, p. 425.

† British Patents Nos. 20,470, Sept. 10, 1913 and 2838, Feb. 3, 1914.

‡ J. S. C. I., 1915, 71.

§ British Patents Nos. 12,653, May 22, and 18,923, Aug. 21, 1914.

|| J. S. C. I., 1915, 707.

¶ U. S. Patent No. 1,168,404, Jan. 18, 1916.

or cobalt to a sintering temperature with small amounts of carbon and aluminum, magnesium or cerium to reduce the metallic compounds. The metallic catalyst thus formed retains its efficiency in continued use for cracking oils for a considerable time.

For the production of light hydrocarbons from heavier oils and the like, **Sabatier** and **Mailhe** \* recommend a two-stage method as follows:

First stage: The vapors coming from solid or liquid hydrocarbons to be treated are directed against wires or metal blades rendered incandescent by an electric current. The liquid to be converted, or its vapor, is brought into contact with them either alone or mixed with hydrogen or any gas rich in hydrogen. Wires of various metals can be employed, either platinum or metal of the platinum series, iron, copper, cobalt, tantalum or any wires that can be rendered incandescent by an electric current of any kind, or wires covered with catalyzing metals or oxides, such as oxides of thorium, zirconium, uranium, titanate acid or mixtures of these oxides. The temperature of the wires is raised by the passage of electric current from 300° to dark or bright red. The dissociation of hydrocarbon products into more volatile hydrocarbon products is the more complete, the greater the length of contact of the wires, or the surface of the catalyzing metals, or catalyzing oxides heated by wires through which an electric current is passing. The output of volatile liquid products and of gas is the greater, the higher the temperature. At the outlet of the apparatus in which the kerosene or heavy petroleum oils, have been exposed to the catalytic action, condensing apparatus is provided to cool the products of the reaction which comprise: 1. Hydrocarbon gases mixed with hydrogen, which can be utilized either directly for heating and lighting, or for explosion engines, or as compressed gases for lighting or for the manufacture of hydrogen by destructive distillation. 2. Liquid hydrocarbons distilling below 150°, containing non-saturated oxidizable hydrocarbons which are treated in the second stage. 3. Liquid hydrocarbons distilling between 150° and 300°, which can either be mixed again with the original raw material, in order to be submitted to a new treatment, or submitted to the action of the second stage in order to render them suitable for lighting purposes. 4. Liquid or solid products which do not distil under 300°, and which must be mixed again with the original raw material, in order to be submitted to a new treatment. 5. Solid carbon substances which are separated.

Second stage: The liquids which are volatile under 150°, as well as those which distil between 150° and 300°, are constituted for the greater part of non-saturated oxidizable hydrocarbons, which can be utilized immediately for explosion engines, lighting, etc., or converted into saturated hydrocarbons which are practically non-oxidizable in the air, by direct hydrogenation of their vapors by means of divided nickel or similar metals. In order to carry out this second stage, hydrogenation may be effected by using, in place of divided nickel or similar metals, a nickel wire, blade or tube arranged in the form of a spiral or net work, heated to a temperature between 200° and 350° by the passage of an electric current. Cobalt, copper, iron, platinum, or metals of the platinum series may be similarly employed. Divided nickel, copper, cobalt, iron, obtained by the reduction of their oxides; platinum in its various forms, or metals of the platinum group, supported on a metallic conductor also are recommended.

\* U. S. Patent No. 1,124,333, Jan. 12, 1915; Chem. Abs., 1915, 710. French Patent No. 475,303, Feb. 4, 1914; J. S. C. I., 1916, 34.

**Sabatier** and **Mailhe**,\* in their process of cracking oils by passing oil vapors over a catalyst at temperatures between 400° and dark red heat, prepare the catalyst of finely-divided metal or metals, or metallic oxides or salts that can be reduced to form divided metal, together with neutral refractory substances free from silica and an agglutinant free from silica.

Suitable refractory materials are magnesia, alumina, bauxite, lime, baryta, strontia, or the corresponding carbonate, or graphite. Suitable agglutinants are glue, dextrin and starch. Examples of such compounds comprise: (1) iron filings, magnesium oxide and dextrin; (2) oxide of iron, magnesium, bauxite and glue; (3) finely-divided iron, alumina and dextrin. The resulting compounds are moulded and dried and packed into cracking tubes composed of metal or earthenware lined with a non-siliceous coating. When the catalyst loses its activity by reason of the deposition of carbon, it is revived by the passage of steam, a gaseous mixture of hydrogen, carbon monoxide and carbon dioxide being produced. This gas can be utilized as a reducing agent or fuel, the carbon dioxide being removed by washing if necessary. The metallic oxide formed by the steam, and the oxide used in making the catalyst initially, are reduced to metal by means of hydrocarbon vapors. The volatile portion of the products of the cracking operation, namely, that distilling below 150°, is treated for the removal of the malodorous unsaturated compounds by reduction with hydrogen in the presence of finely-divided metals at 150° to 300°.

**Hall** † cracks oils for the manufacture of motor spirit by heating the vapors of the heavy hydrocarbons under pressure in the presence of a catalyst capable of affixing hydrogen to hydrocarbons, then allowing the vapors to expand and deposit carbon, and finally condensing the vapors with or without preliminary dephlegmation or subsequent distillation.

The operation may be conducted under a pressure of five atmospheres and at a temperature of 600° and upwards. Gas oil treated in this way yields 50 to 70 per cent of oil of sp.gr. 0.765 suitable for gasoline engines. Metals such as nickel, cobalt, silver, palladium, chromium or manganese, or their oxides, may be used as catalysts. In one form of apparatus the oil passes through a preheater into a converter consisting of tubes containing cylindrical nickel rods, and the products escape through a reducing-valve into an expansion chamber, fitted with a metallic gauze screen and thence to a condenser.

The unsaturated materials formed during the process are claimed to be saturated with hydrogen which is derived from the oil itself. No water, steam, hydrogen or outside source of hydrogen is used.‡

In a paper by **Hall** on the cracking of oils read before "The Institution of Petroleum Technologists," 1914, the utility of steam as a source of hydrogen in cracking processes involving passing oil through heated tubes, is discussed by Hall, who states:

\* British Patent No. 16,791, July 14, 1914; Chem. Abs., 1916, 273; U. S. Patent No. 1,152,765; Chem. Abs., 1915, 2814.

† British Patent No. 17,121, July 25, 1913; J. S. C. I., 1914, 1149. See also U. S. Patent No. 1,261,930, April 9, 1918; Chem. Abs., 1918, 1597.

‡ U. S. Patent No. 1,175,909, March 14, 1916.

"As far as any advantage from the use of water as a hydrogenating agent is concerned, I am sure it is nil, whether with or without a catalytic combiner, and I have operated fair-sized apparatus for weeks with nickel and other so-called catalyzers, first with and then without water, and we could never notice any material difference. If hydrogen without oxygen is utilized, better results are obtained, but the expense appears to be prohibitive. With nickel rods in the tubes, and with water used with the oil, I have found the rods so heavily coated after a six- or eight-hour run, that the coating could only be removed by buffing. It was impossible in any way to wipe it off. The substitution of copper for nickel rods gave equally good results. In large tubes, 1 in. or more, water in excess of 8 per cent or 10 per cent is utterly impracticable, if the process is conducted under pressure, and at any rate of feed that would be commercially economical, as no uniform pressures can be maintained."

Hall further states that \* the admixture of water or steam with the oil during cracking neither prevents decomposition of carbon nor promotes hydrogenation of the unsaturated hydrocarbons. The latter, in large proportion, are objectionable in cracked spirit mainly because of the resinous carbon colloid with which they are usually associated and which, by oxidation, tends to form a varnish-like product detrimental to the working of motor engines. Owing to the combination effected in the compressor between the condensable vapor and the fixed gases, the spirit obtained by Hall's method is stated to be largely free from this objection.

By another modification of the Hall process † motor spirit is produced by passing a kerosene fraction boiling up to about 220°, from which the gasoline has been removed, between minute interstices under very high pressure, such as 1000 to 3000 lb. per square inch, in the presence of hydrogen, coal gas, or other gas containing free hydrogen or a hydrocarbon gas such as ethylene or oil gas, and at a temperature not above the lowest boiling-point of the liquid, e.g., 100° to 120°. Combination of the gas and oil is said to take place. Suitable apparatus comprises a series of discs or plugs, preferably nickel between or through which the liquid is forced. The discs or plugs may be scratched to form fine grooves.‡

Lamplough § comments on the relative value of various catalysts employed in bringing about reaction between the vapors of oils and water.

He states that burnt clay or aluminum silicate, which has frequently been recommended, is very slow in action and is open to the objection that the clay is apt to become clogged by deposition of tarry masses which can be removed only with great difficulty. The use of iron as a catalyzer is stated to be open to the objection that if the water vapor is used in excess the iron will rust and become unsuitable for use. Nickel in the form of fine particles is similar to clay with respect to becoming coated with particles of tarry or carbonaceous matter. On the other hand nickel in the form of a compact metal has been found by test to remain free of carbon deposits, while exhibiting the desired catalytic effect.

\* J. Inst. Petrol. Techn., 1915, 1, 147; J. S. C. I., 1916, 296.

† British Patent No. 103,720, Mar. 4, 1916; Chem. Abs., 1917, 2043.

‡ See French Patent No. 481,066, Feb. 25, 1916.

§ U. S. Patent No. 1,229,098, June 5, 1917.

A fuel suitable for use in automobile engines is obtained by **Higgins** and **Preston** \* from heavy hydrocarbon oils by heating them in a converter under pressure to a temperature sufficient to volatilize the heaviest constituent of the oil, passing the vapors alone or with hydrogen gas over a catalyst, and condensing them in contact with the catalyst. The apparatus comprises a converter fitted with a pressure-regulating valve which is kept closed until the requisite temperature is reached. After the valve is opened, the vapors, together with hydrogen admitted into the converter, pass to a condenser which contains a cartridge of catalyst. The catalyst may consist of nickel oxide and pumice stone. The process may be applied to the treatment of shale oil, crude benzene, crude naphtha, crude tar oil, or paraffin oil, or to mixtures of crude benzene with crude naphtha, paraffin oil, or coal-tar oil.

A process of making gasoline from heavier oils by cracking is described by **Low**. †

In one form of this process the oil to be cracked is sprayed into contact with a heating element which may carry a catalytic body. Iron, nickel, cobalt and copper are mentioned for this purpose. The spraying operation may be carried out in a closed vessel in an atmosphere of hydrogen or blue water gas. Under such conditions it is stated that unsaturated compounds may be converted into saturated compounds. A hot nickel surface in a hydrogen-containing atmosphere is particularly advantageous in causing the formation of saturated gasoline from heavy oils projected against such surface.

According to a process devised by **Wells** ‡ directed to the production of gasoline from heavier petroleum products, oil vapors are conducted into a bath of molten lead, which is heated to about 480° to 540° C. and violently agitated by mechanical means at the moment of contact. §

**Wells** || also recommends the following cracking process: Preheated kerosene or a heavier petroleum oil is fed through a hot cracking chamber filled with jackstones coated with nickel or other catalyst and the crude gasoline thus formed is preferably refined by a further treatment with hydrogen and a catalyst at a temperature of about 240°.

In cracking petroleum oils in the presence of hydrogen, **Whitaker** and **Leslie** ¶ have reached the following conclusions:

1. That effects often ascribed to catalysis are in reality due to effective heat transfer by conduction and convection from the large heated surfaces exposed to the gases.
2. That hydrogen is produced from an oil even when the cracking takes place in hydrogen.
3. That considerable absorption of hydrogen takes place when an oil is cracked in an atmosphere of hydrogen, and this absorption is greater the

\* British Patent No. 23,876, Dec. 10, 1914; Chem. Abs., 1916, 1594.

† U. S. Patent No. 1,192,653, July 25, 1916.

‡ U. S. Patent No. 1,187,874, June 20, 1916.

§ J. S. C. I., 1916, 883.

|| U. S. Patent No. 1,248,225, Nov. 27, 1917.

¶ J. Ind. Eng. Chem., 1916, 694.

higher the concentration of hydrogen, the higher the temperature (within the range studied), and the lower the oil rate.

4. That no marked and consistent difference in the amount of tar formed when an oil is decomposed alone or in hydrogen at temperatures of  $723^{\circ}\text{C}$ . or below is noticeable. At  $825^{\circ}\text{C}$ . less tar is formed when the oil is cracked in hydrogen. The tars formed below  $723^{\circ}\text{C}$ . are in large part unchanged or partly changed oil, whereas those tars formed above  $800^{\circ}\text{C}$ . are essentially composed of synthetic products.

5. That the reactions which result in decreasing the proportion of illuminants are the most rapid.

6. That the presence of hydrogen during the decomposition of an oil has the effect of increasing largely the proportion of the carbon of the oil appearing as hydrocarbons in the gas.

7. That with correct design of apparatus, and proper adjustment of temperature, rate of oil feed, and concentration of hydrogen it is possible to obtain gases of widely varying compositions.

A method of cracking heavy hydrocarbons in the presence of hydrogen, proposed by **Bergius**\* involves treatment in an autoclave at a temperature below  $500^{\circ}$  and under a pressure of over 20 atmospheres in order to obtain light hydrocarbons in the form of saturated benzine.† As an example, 11 kilos. of gas tar are heated with hydrogen at 100 atmospheres pressure, to  $400^{\circ}\text{C}$ . After four hours the mass is distilled at about  $250^{\circ}\text{C}$ ., and about 60 per cent of distillate resembling petroleum oil is obtained, which can be further treated by rectification.‡

A most interesting and ingenious method of hydrogenating coal is described by **Bergius** and **Billwiller**.§ These investigators find on heating coal with hydrogen to a temperature between  $300^{\circ}$  and  $500^{\circ}\text{C}$ ., involving pressures up to 200 atmospheres, the hydrogen combines with the coal, forming hydrocarbons which are liquid at ordinary temperature or have a low melting-point. Only a very small amount of methane is produced. Thus, they obtain distillates from coal amounting to nearly 100 per cent of the carbonaceous substance, whereas by the usual method of distilling coal the liquid products usually do not exceed 3 per cent. The nitrogen contained in the coal is transformed into ammonia. Some bodies of the phenolic type are produced. The reaction is shortened if a solvent such as benzene is employed. The process is applicable to the treatment of

\* Austrian Patent No. 71,208, June 26, 1916; French Patent No. 470,551, Apr. 6, 1914; J. S. C. I., 1915, 167.

† British Patent No. 5,021, Mar. 31, 1915. Addition to 18,232 of 1914; J. S. C. I., 1916, 167, 732.

‡ J. S. C. I., 1915, 862.

§ U. S. Patent No. 1,251,954, Jan. 1, 1918.

wood, peat, tar and pitch in like manner. Bergius and Billwiler give several illustrations of the method of procedure, the following being noted:

1. 400 kg. powdered coal are filled into a pressure-resisting vessel of about 400 liters capacity, which is connected to a tank in which hydrogen is held under 200 atmospheres pressure. After fifteen hours the connection with the hydrogen tank is turned off and the vessel is emptied. About 10 to 15 kg. of hydrogen have then been consumed, according to the quality of coal used. From the contents of the vessel more than half of the coal can be separated from solid residue as liquid. The remaining part of liquid products in the solid residue can be gained by extraction.

2. 150 kg. powdered coal are placed with an equal quantity of heavy benzene in a pressure-resisting vessel of about 400 liters capacity, connected to a hydrogen tank. For the purpose of mixing, the vessel is rotated. After twelve hours, at a temperature of 400°, the vessel is opened and the liquid produced is separated from the solid residue. Only 15 per cent of the weight of coal employed is then left. The remaining 85 per cent is dissolved in the benzene. The consumption of hydrogen is about 5 kg.

One modification of a method of cracking oils used by Ellis \* involves passage of the raw oil material, such as kerosene, through a heated zone containing catalytic bodies, in the presence of added gases derived from the decomposition of oil which has previously passed through the cracking zone. In another modification † kerosene or other oils heavier than gasoline are decomposed by heating in a series of superposed nearly horizontal pipes. The temperature of the oil is gradually increased as it passes through the pipes and after the maximum cracking temperature desired has been attained the heating is continued in the presence of catalytic material at a gradually decreasing temperature until the products have assumed a state of stable equilibrium. The gasoline is then condensed.

An apparatus described by the Standard Oil Co.‡ for converting heavy hydrocarbons into gasoline and other light oils § consists of a still containing catalytic plates suspended in the vapor space, or interlocking downwardly convex plates supported by hinges and extending over the bottom of the still in such a manner as to provide for the circulation of the oil. The catalytic surfaces may consist of copper, brass, steel, or other metal in the form of solid plates or gauze plates; plates of mineral fibres such as asbestos or glass may also be used.

\* U. S. Patent No. 1,216,971, Feb. 20, 1917.

† U. S. Patent No. 1,249,278, Dec. 4, 1917.

‡ British Patent No. 7,541, Oct. 20, 1914; Chem. Abs., 1916, 2798.

§ Using the process described in British Patent No. 29,862, 1912; Chem. Abs., 8, 2058.

The use of sulphur to promote the cracking of heavier oils to yield lighter products such as naphtha or benzine is suggested by Day.\*

He states that by adding sulphur or a sulphur compound to crude oils or distillates containing little or no sulphur such oils can be more easily decomposed by heat under the proper pressure with the production of an increased yield of distillates lighter in specific gravity than those which would be produced by the ordinary process of simple distillation. It is also stated that the distilling operation may be carried out in the presence of a hydrogen-containing gas and a catalytic agent or porous contact substance in the manner previously proposed by Day (see pages 10 and 20). The sulphur may be added to the oil in the form of the sulphide of ammonium, sodium, iron or copper or as hydrogen sulphide. Sulphates are not applicable for use in this process. A perforated supply pipe, see Fig. 56c, for admitting oil and gas

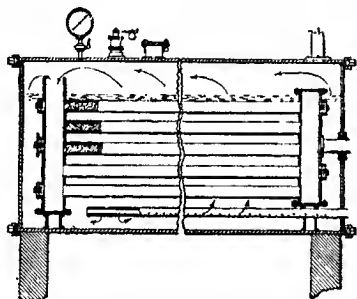


FIG. 56c.

is placed near the bottom of the still. Hydrogen and hydrogen sulphide may be admitted at this point. Contact material in the tubes above the perforated pipe may be iron pyrite, hydrogen, zinc dust, reduced nickel or cobalt, dry porous clays, spongy platinum, or palladium. Day states he has found that the cracking operation is greatly aided by passing a hydrogen-carrying gas or vapor, such as hydrogen sulphide, ammonia, illuminating gas, or water gas, or steam through the oil and thence passing the commingled oil vapors and hydrogen from the space above the oil through porous adsorptive contact material. A catalytic action here takes place, the hydrogen being combined with the previously unsaturated hydrocarbons, resulting in the production of oils having a lower specific gravity and lower boiling-point.

As examples of the carrying out of this process, Day states that he placed 100 cc. of crude petroleum in a retort, and first distilled off the distillate obtainable by the ordinary course of distillation obtaining on the average 3 per cent of distillate, distilling below 150° C., 20 per cent of distillate distilling between 150° and 300° C., in the case of Mexican oil from well No. 4 of the Potrero del Llano district, Mexico, Province of Vera Cruz, and determined that the distillates, even the 3 per cent of naphtha distilling below 150°, had a burnt and objectionable odor and would be characterized by more than 50 per cent of unsaturated hydrocarbons. With another portion of the same crude oil, the distillation was repeated, using 5 to 10 per cent of sulphur. The result was an increase up to

\* U. S. Patent No. 1,221,698, Apr. 3, 1917.



from 7 to 10 per cent in the yield of naphtha and up to 30 to 35 per cent of burning oil, the distillate between 150° and 300° C., having a very marked improvement in the odor, as soon as the sulphuretted hydrogen accompanying these distillates was removed by the addition of a dilute solution of soda. By the treatment of the first distillate obtained, without the addition of sulphur, with sulphuric acid it was impossible to obtain a water white oil; the distillate obtained with the use of sulphur was quite easily refined. Both samples were tested as to the content of unsaturated hydrocarbons, and it was found that the distillate between 150° and 300° C., by the ordinary process contained over 50 per cent of unsaturated hydrocarbons. The test was carried out by shaking the distillate for fifteen minutes with an equal volume of sulphuric acid of 1.84 gravity. This test when applied to the oil from the sulphur distillation, showed less than 20 per cent of unsaturated hydrocarbons. These experiments were carried out on a larger scale in iron stills in the laboratory of an oil-refining company with similar results.

To convert hydrocarbons of high boiling-points into products of low boiling-points, **Rostin and Forwood** \* suggest that a heavy hydrocarbon, in the form of vapor, be mixed with hydrogen sulphide and brought into contact with a substance such as heated copper capable of liberating the hydrogen of the hydrogen sulphide. The nascent hydrogen combines with the vapors of any unsaturated hydrocarbons produced. The copper sulphide arising from the operation may be treated with gases rich in hydrogen, forming hydrogen sulphide and copper.

The **Simplex Refining Co.**† describe a cracking process in which heavy petroleum oil is made to circulate, with or without pressure, in a continuous cycle, through serpentine tubes, which are heated to the cracking-point of the oil, and means are provided for the continuous withdrawal of the resulting vapor and the addition of fresh oil to keep the circulating oil at a constant volume. A portion of the condensed light vapor is injected into the residue when it returns to the heating vessel. Advantages claimed for the process are regularity in working, and the prevention of overheating and formation of carbonaceous and viscous deposits within the tubes.

Aromatic compounds are prepared by dehydrogenation of petroleum oils according to **Mann and Chappell**.‡ The amount of benzol, toluene, xylene and other aromatic compounds in petroleum oil is increased by heating the oil in retorts to 600° to 750° under a pressure 1 to 4 in. below atmospheric pressure in the presence of 500 to 800 cu. ft. of air for each 15 to 20 gals. of oil under treatment, using a lower oxide of nickel as a catalyst. Iron or copper oxides also may serve as catalysts. The catalytic oxides are prepared from the corresponding nitrates using a support of pumice stone or fire brick.§

An apparatus for treating heavy oils and involving the hydrogenation of light oils which are produced in the operation has been devised by **Brown**.||

\* British Patent No. 107,034, May 15, 1916. See also Chem. Abs., 1918, 1558; Danish Patent 22,824, February 18, 1918.

† French Patent No. 480,147, November 8, 1915; J. S. C. I., 1917, 127.

‡ U. S. Patent No. 1,214,204, Jan. 30, 1917; Chem. Abs., 1917, 1039; J. S. C. I., 1917, 332.

§ See also U. S. Patents Nos. 1,249,444, Dec. 11, 1917, and 1,257,906, Feb. 26, 1918.

|| U. S. Patent No. 1,225,569, May 8, 1917.

The apparatus is shown in Fig. 56*d*, in which *a* is a still or boiler where the oil to be treated is placed. A pipe *b*, which extends to the bottom of the still, is used for the introduction of hydrogen. The vapor produced by heating the oil is mingled with hydrogen and passes through a vertical conduit in which are mounted perforated nickel plates *c*<sup>1</sup>. These are supported by central rods *c*<sup>2</sup>. In the upward passage of this vapor and hydrogen, contact with the surface of the nickel is brought about and it is claimed that the catalytic action of nickel is thus utilized. The volatile products obtained from the process are passed to a condenser. A water-cooling device *g* is placed about the conduit *c* in order to maintain the temperature sufficiently low to condense vapors of heavy oil, this condensate being returned to the still or boiler.

The cracking of gas oils in various atmospheres has been investigated by **Downing and Pohlman**.<sup>\*</sup> The atmospheres used were nitrogen, carbon dioxide, carbon monoxide, hydrogen, methane, blue gas, and a mixture of blue gas with 10 and 20 per cent of steam, respectively. The effect of each diluent on candle-power and the production of gas, tar, and carbon was studied.

The application of a high-tension electric discharge for the purpose of increasing the proportion of fixed gases, in gases or vapors obtained by the cracking of oils has been proposed by **Davidson and Ford**.<sup>†</sup>

They state that the constitution of the hydrocarbon constituents in a gas of this character may be materially changed by the action of the electric discharge, the general effect being the formation of bodies of less molecular weight which are not condensable, thus increasing the proportion of fixed hydrocarbon constituents of the gas as compared with the other components, such as hydrogen or carbon monoxide. In tests which were made the amount of methane in the gas was increased from 25 per cent to about 40 per cent, while the amounts of  $C_nH_{2n}$  were increased from between 7 and 10 per cent up to 20 and 23 per cent. In carrying out this process, apparatus which is similar to that used for the electrical precipitation of suspended matter from gases may be employed.

**Cherry** ‡ describes a method for the production of hydrocarbon compounds by a synthetic process involving the use of a high-frequency electric current. Cherry states that a rearrangement of the molecular structure of a hydrocarbon can be brought about to change the boiling-point and gravity, by subjecting the hydrocarbon to the silent discharge of a bipolar oscillatory high-frequency electric current and the boiling-point and gravity of the compound produced can be varied by varying the frequency of the current applied; and furthermore, a relatively low-grav-

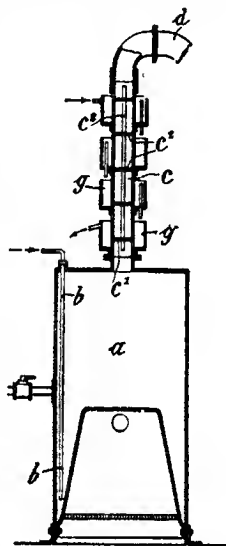


FIG. 56*d*.

<sup>\*</sup> Am. Gas. Inst. Gas. J., 1917, 137, 24-26; J. S. C. I., 1917, 125.

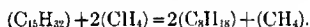
<sup>†</sup> U. S. Patent No. 1,229,042, June 5, 1917.

<sup>‡</sup> U. S. Patent No. 1,229,886, June 12, 1917.

ity hydrocarbon can be so changed as to produce a compound of higher gravity and of lower boiling-point by subjecting such low-gravity compound to the electric discharge when the low-gravity hydrocarbon is in a vaporized state and mechanically mixed with a small proportion of a high-gravity low boiling-point hydrocarbon while a high-gravity low boiling-point hydrocarbon (such as casing head gasoline) can be so changed as to produce a product of lower gravity and higher boiling-point, by the action of the electric discharge while the high-gravity hydrocarbon is in a vaporized state and mechanically mixed with a small proportion of a relatively low-gravity high boiling-point hydrocarbon.

In practicing Cherry's process, the vaporized or gaseous hydrocarbon material is passed through a bipolar oscillatory high-frequency silent electric discharge, and a rearrangement of the molecular structure is stated to be thereby brought about to either increase or decrease the proportion of hydrogen in the resulting compound without the waste incident to destructive distillation. The vaporized or gaseous hydrocarbon may be passed through a peculiar electric field or an electric treating chamber provided with separated electrodes between which the hydrocarbon body flows so that this body will be subjected for a more or less extended period of time to the silent electrical discharge oscillating back and forth between the electrodes.

As an example of the application of the method to hydrocarbon compounds of the paraffin series, one volume of pentadecane ( $C_{15}H_{32}$ ) is introduced into a still, to every two volumes of methane ( $CH_4$ ) and the mixture of the resulting vapor and gas rising from the liquid in the still is passed through an electric field under proper heat and pressure conditions, a resulting liquid product being drawn from a condenser consisting of octane while the excess of methane is separately collected. In this instance, approximately the following reaction is claimed to take place.



**Hirt** \* subjects petroleum oil to an electric arc in the presence of hydrogen under pressure. Oxygen or steam may be introduced to remove carbon deposits.

**Coast** † mixes petroleum oil, natural gas and steam and subjects the mixture to pressure at a cracking heat. By mixing the steam and gas with the oil, a much "sweeter" and better product (gasoline) is obtained and the yields are found to be improved.

Heavy oils, kerosenes and petroleum residues, are converted into gasoline and other volatile oils by distilling in a still in which hydrogen is injected into the oil by a pipe, and then passing the resulting mixture of oil vapor and hydrogen over nickel plates, the operation being effected under a pressure, e.g., five to ten atmospheres. The nickel plates consist of perforated discs held in position in a vertical pipe by a central rod. The vertical pipe may also be lined with nickel. A cooling-system surrounding this pipe ensures the return of heavy oils to the still.‡

\* U. S. Patent No. 1,250,879, Dec. 18, 1917.

† U. S. Patent No. 1,252,401, Jan. 8, 1918.

‡ Dampierre, British Patent No. 109,796, Aug. 15, 1917; Chem. Abs., 1918, 222. French Patent No. 478,831, Feb. 22, 1915 and Addition No. 20,331, Aug. 1, 1917; Chem. Abs., 1916, 10, 2297 and 1918, 12, 1121.

The hydrogenation of petroleum is carried out by **Thompson** in the following manner:\* A catalyzer is prepared by reducing the oxide, nitrate, carbonate, acetate or formate of nickel by hydrogen at a temperature of 320° to 350° C., for one-half to one hour. The catalyzer is added to the hydrocarbon which is heated in a cracking still and purified water gas or pure hydrogen is passed through in large volume with strong pressure and agitation. The resulting mixture of gases and vapors is passed to condensers and the residual gases may be used again, if considerable hydrogen is present. As the above method of making the catalyzer gives a pyrophoric product, the reduced material should be mixed with oil and pumped to the still to avoid oxidation.

Another method of preparing the catalyzer is: mix nickel formate with petroleum oil and pass the mixture into the still while injecting a strong current of water gas. The passage of the gas through the oil serves to agitate the contents of the receptacle and the agitation may be further supplemented by a stirrer. Thompson states that the formate is decomposed, leaving the nickel in an almost colloidal state of fineness in the oil. An amount of catalyzer up to 2 per cent may be employed. The catalyzer is recovered from the still residue by washing with benzol.

Tests conducted by **Cross** † with many catalytic bodies including aluminum powder, nickel, copper, mercury, zinc dust, iron dust, and platinized pumice did not afford increased yields of light hydrocarbons from heavier oils.

**Rittman** observes that many inventors have made claims to processes of hydrogenation of petroleum oils in connection with their method of "cracking." In most of these cases the hydrogen is derived from steam which is admitted with the oil or else is derived from the hydrocarbons themselves by employing a suitable catalyzer.‡

**Jolicard** § states that aromatic hydrocarbons are produced when coal is treated at 400° C. with nascent hydrogen in a furnace, which is not heated externally. The hydrogen may be produced for example by introducing a mixture of superheated steam and air at 500° C.; or carbon monoxide (producer gas, water gas) at 600° C. may be used in place of all or part of the air. A gaseous catalyst, such as chlorine or hydrochloric acid, may be introduced, or a solid catalyst, such as copper or nickel, may be deposited on the coal.

\* U. S. Patent No. 1,160,670, Nov. 16, 1915.

† Petroleum, Asphalt and Natural Gas, Bulletin No. 14, Kansas City Testing Laboratory, 97.

‡ Bulletin 114, Bureau of Mines, 20.

§ French Patent No. 475,433, Feb. 17, 1914; J. S. C. I., 1916, 36.

**Zerning**\* passes a mixture of heavy petroleum and water (1 part water to 6 to 10 parts oil) first through a heater to raise the temperature of the mixture to 300° to 400° C., then through tubes at a dull red heat, condenses and passes the gases from the condensers under pressure into a body of petroleum at ordinary temperature, from which gasoline is subsequently recovered by distillation.

**Cracking Tars and Oils.** Tars and mineral oils are treated for the production of benzene, toluene, essences, etc., by heating them in a closed vessel under pressure and allowing the vapors formed to expand when the requisite temperature and pressure have been reached. In the case of tar, temperatures between 90° and 450° and pressures between 2 and 18 kg. per square centimeter are used. The vapors obtained in one autoclave may be injected into a second autoclave containing tar or oil under a different pressure and temperature. The finely-divided nascent carbon which separates acts as a catalyst, the nascent hydrogen also entering into reaction.†

The residue from the manufacture of oil gas may be treated directly with hydrogen to form new hydrocarbon compounds which are capable of further decomposition.‡

In some experiments made by **Davidson**§ on the heat decomposition of a mixture of ethane and propane from natural gas it was found that the metals nickel, iron and cobalt hindered the production of aromatic hydrocarbons but promoted, to a marked degree, the formation of hydrogen and carbon.

\* U. S. Patent No. 1,183,266, May 16, 1916.

† *Soc. Lyonnaise des Eaux et de l'Eclairage*. British Patent No. 9,728, July 3, 1915; Chem. Abs., 1917, 95.

‡ Rinker, Canadian Patent No. 182,104, Feb. 5, 1918; Chem. Abs., 1918, 763.

§ J. Ind. Eng. Chem. 1918, 901.

## CHAPTER XIX

### THE HYDROGEN PROBLEM IN OIL HARDENING

Oleic acid and hydrogen combine, molecule for molecule, to yield stearic acid according to the reaction:



Thus 282 pounds of oleic acid require 2 pounds (or about 0.7 per cent) of hydrogen for the production of 284 pounds of stearic acid, and similarly the transformation of olein into stearin requires the use of about 0.68 per cent hydrogen.\*

One thousand cubic feet of hydrogen weigh approximately 5.6 pounds, hence a pound of olein calls for a little over 0.1 of an ounce of hydrogen equivalent to approximately 2500 cubic feet of hydrogen per ton (of 2000 pounds) of olein. Thus by weight only a relatively small quantity of hydrogen is needed, while by volume the amount required, of course, is considerable.†

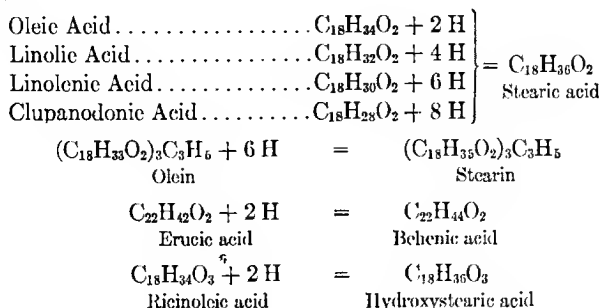
\* The amount of hydrogen required for complete conversion is given by Sachs (Zeitsch. f. angew. Chem., 1913, 94, 784) as 7.4 kilos or 85 cubic meters hydrogen per 1000 kilos oleic acid. 1000 kilos of linoleic acid having two double bonds call for 14.2 kilos, or 170 cubic meters of hydrogen. 1000 kilos of linoleic with three double bonds need 21.6 kilos, or 259 cubic meters of hydrogen, while a like weight of clupanodonic acid with its four double bonds requires 29 kilos, or 348 cubic meters of hydrogen. The hydrogen requirements per ton of some of the fats enumerated by Sachs are as follows:

	Cubic meters
Cocoonut oil. . . . .	7.8
Tallow. . . . .	33.57
Olive oil. . . . .	68.80
Oleic acid. . . . .	88.80
Corn oil. . . . .	143.75

Dr. Holde observes (Seifen. Ztg. (1912), 918) that oleic acid, the most important constituent of all semi-drying liquid oils, requires only 2 parts of hydrogen to 282 parts of oil in order to get stearic acid, while linoleic and linolenic acid require 4 and 6 parts respectively to 280 and 278 parts. Ricinolic acid, which contains one atom of oxygen more than oleic acid, forms an oxystearic acid which has a very high melting point, but which also only contains 2 atoms more of hydrogen than the original acid. The glycerides of stearic or palmitic acid naturally remain unchanged throughout the operation.

† According to Linde (Production of Hydrogen, Third Int. Cong. of Refrigeration, 1913) six to ten cubic meters of hydrogen are required for hardening one hundred kilos of oil.

The following tabulation shows the nature of the reaction in several cases:



One of the problems in the hydrogenation field is that of a cheap supply of pure hydrogen. The demand for hydrogen in various directions has increased of late and undoubtedly this will lead to improvements in the manufacture of the gas.

The two methods now most favored in the hydrogenation of oils are the iron-sponge steam process and the electrolytic method. For large plants the iron-sponge steam process is preferred, but it is relatively complicated and scarcely to be recommended for plants calling for 1000 cubic feet of hydrogen, or less, per hour.

In the electrolysis of brine to make caustic soda and bleach, there exists a by-product of hydrogen sufficient in amount to treat an enormous quantity of oil. To-day a good portion of this hydrogen is allowed to go to waste. Eventually it may be used, to some extent at least, for hydrogenation purposes. One electrolytic plant in this country is producing about one ton of hydrogen daily. Another plant generates nearly one-half a ton, while a third concern discharges into the air nearly 300,000 cubic feet each day.\* In spite of the vast

\* Similar conditions exist abroad, Blum reporting (Met. and Chem. Eng. (1911), 157) that enormous amounts of hydrogen gas are produced in the large works for the production of caustic soda and chlorine by electrolysis of common salt solutions. The hydrogen gas is set free together with the caustic soda at the cathode. The quantities are so large, compared with the demand which exists at present for hydrogen, that most of the hydrogen gas is passed unused into the air. The Griesheim-Elektron Company in Germany produces daily 20,000 cubic meters of hydrogen of about 90 to 97 per cent purity. In this case the cost of the gas is practically that of its compression and storage. Special railway cars are built in Germany for the transportation of 500 cylinders containing 2750 cubic meters of hydrogen gas. The cost of shipment of the cylinders is so great that the distribution, of course, is only local, as regards consumption on the large scale. The Zeppelin Garage in Frankfort is supplied with hydrogen by means of a high-pressure main from Griesheim.

amount of by-product hydrogen obtainable, it appears that oil manufacturers prefer to install hydrogen-generating equipment in their present works, rather than to ship oil to a source of waste hydrogen and conduct hardening operations at some relatively remote point.

In consequence the present methods of preparing hydrogen are being carefully scrutinized and new systems for the generation of the gas are being studied and developed. For this reason the whole subject of the production of hydrogen is here reviewed at some length,\* the proposed technical methods for its generation being classified as follows:

- A. *Water gas as a source of hydrogen.*
  1. Replacement of carbon monoxide<sup>†</sup> by hydrogen.
  2. Liquefaction and other methods for the removal of carbon monoxide.
- B. *Decomposition of hydrocarbons.*
- C. *Action of steam on heated metals.*
- D. *Wet processes and the decomposition of hydrates.*
  1. Action of acids on metals.
  2. Decomposition of water by miscellaneous chemicals.
  3. Electrolysis of water.
  4. By-product hydrogen.

The hydrogen problems involved in the hydrogenation of oils are discussed by **Walter** † who states that a plant for oil hardening cannot well be installed by small concerns, but only by those having powerful financial resources, because the cost of equipping for an adequate supply of hydrogen represents so great an outlay. If water gas or coke oven gas containing 40 to 50 per cent hydrogen could be used the matter would present a different aspect. Water gas contains on the average:

	Per cent
Hydrogen .. . . . . .	50
Carbon monoxide. . . . .	41
Carbon dioxide. . . . .	4
Nitrogen. . . . .	4.5
Methane. . . . .	0.5

A plant for the manufacture of water gas is much cheaper than one for making technically pure hydrogen. Reckoned on the hydrogen content the cost of production of water gas is very much lower than that of pure hydrogen.

\* **Brahmer**, *Chemie der Gase*, Frankfort, 1911, contains much useful information on the production of hydrogen. The subject of hydrogen production on a commercial scale is treated by **Lepsius** in *Moniteur Scientifique*, 1912, 493-500.

† *Seifen. Ztg.* (1913), 4.



Coke oven gas contains about the following:

	Per cent
Hydrogen.....	46
Nitrogen.....	15
Carbon monoxide.....	7
Methane.....	20
Ethylene.....	2
Carbon dioxide.....	4

This gas may be obtained in large quantities at low cost in the neighborhood of coke oven plants. Many of the patents relating to the hydrogenation of oils refer to the use of gas mixtures containing hydrogen as well as to hydrogen gas in a pure state. These statements, Walter argues, appear apparently only as a precaution in order to preclude others from making application for patent protection on the use of hydrogen-containing gases in the place of pure hydrogen. He regards the investigation of these hydrogen-containing mixtures as never having been properly followed out, but thus far the results obtained are not promising.

Carrying out the hydrogenation process with hydrogen-containing gases involves: (1) the catalyzer must not become contaminated with poisons; (2) the process must proceed in spite of the presence of foreign gases; (3) foreign gases must not injure the oil.

Carbon monoxide and nitrogen in the pure state apparently do not injure the usual catalyzers in the least. As to the remaining impurities the sulfur compounds are catalyzer poisons. It has been noted with water gas that the catalyzer loses its activity much sooner than when pure hydrogen is employed. Foreign gases, which are indifferent in a chemical sense, of course dilute the hydrogen with which they may be mixed, and when one is working with a dilute in place of a concentrated reagent, the action usually is slower. In this connection investigation shows that with increasing dilution of the hydrogen employed, the time required for treatment lengthens, a result which, of course, ordinary practice would indicate is to be expected. Also hardening cannot easily be carried as far with hydrogen-containing gases as with pure hydrogen. It can be stated as a general rule that in oil hardening the hydrogen conducted into the oil is not wholly absorbed, but goes as a stream of gas through or in contact with the oil, so a considerable proportion of the hydrogen introduced is not used. When one is using water gas in place of hydrogen, the former gives up only a portion of its hydrogen to the oil. The hydrogen available to the oil is thus proportionately less than with ordinary hydrogen gas, and repeated conveyance of the partially-used water gas through the oil is as good as useless because of the great reduction in the proportion of hydrogen.

Since only a part of the hydrogen contained in water gas may be utilized, it is necessary to employ relatively a much larger quantity of the latter. Of the 50 per cent or so of hydrogen contained in

water gas, according to Walter, only about one-third or approximately 17 per cent of the total gas is used. To secure the same effect 600 cubic feet of water gas in place of 100 cubic feet of hydrogen are required, in which case about 500 cubic feet of spent gas results. The spent gas, of course, should not be thrown away as this would be wasteful and arrangements must be made for its use in heating, lighting or power applications. It is not always convenient to thus make use of such a large volume of hydrogen-spent gas; furthermore it is necessary to make all the pipes and connections larger by six-fold than when concentrated hydrogen is employed, which means an additional expense.

Finally there is the question as to whether or not the foreign gases \* contained in water gas exert any detrimental influence upon the hardened oil; whether they do not during the process bring about side reactions. As regards carbon monoxide † and carbon dioxide no chemical action on oils or fatty acids under these conditions is known, yet eventually catalyzers may be employed which cause side reactions. If the hardened oil is to be used for technical purposes such reactions probably need not be feared, but for edible purposes this may not obtain. In this connection Bomer has laid down the condition in oil hardening that the hydrogen employed must be pure when the fat is to be used for edible purposes. Thus when using water gas in place of hydrogen, a number of difficulties are likely to arise in large scale operation and the seeming financial advantage on close inspection shrinks considerably, practically leaving the field to technically pure hydrogen.‡

\* The addition of small quantities of a second gas to a pure gas markedly reduces the rate of diffusion in liquids, according to Barus (*Chem. Abs.* (1913), 3871).

† Caro (*Seifen. Ztg.* (1913), 852) considers the presence of carbon monoxide in hydrogen used for hardening fats with nickel catalyzers to be, under some circumstances, injurious to the catalyzer. Maintaining the temperature of the oil during hydrogenation above 200° C. is said to be beneficial, as any nickel carbonyl formed will be at once decomposed at that temperature.

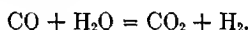
‡ Goldschmidt (*Seifenfabr.*, 32, 713) states that a good and cheap source of hydrogen gas is one of the greatest problems connected with the process; that such impurities in the gas as arsenic, phosphorus, hydrogen sulfide, mineral acids, carbon bisulfide, chloroform and acetone poison catalysts of the platinum group; while sulfur, chlorine, bromine and iodine unfavorably affect those of the nickel group.

Fry states that negative hydrogen has been shown to act as a reducing agent, since it naturally tends to revert to its ordinary state, positive hydrogen, which change is accompanied by the liberation of electrons. (*J. S. C. I.*, 1914, 271.)

## CHAPTER XX

### WATER GAS AS A SOURCE OF HYDROGEN AND THE REPLACEMENT OF CARBON MONOXIDE BY HYDROGEN

Many suggestions have arisen for the production of hydrogen from water gas, involving replacement of the carbon monoxide present by hydrogen through the reaction



Because of the incompleteness of the reaction, those methods proposed which do not take cognizance of the accumulation of carbon dioxide and consequent repression of the progress of the reaction have not been particularly successful. The reaction is a reversible one and unless means are taken to remove the carbon dioxide as formed, the resulting gas mixture contains hydrogen, carbon dioxide and carbon monoxide usually in such proportion as to be too costly of purification for handling on the large scale. In consequence lime or other alkali has been suggested for absorbing the carbon dioxide. These suggestions appear in the patents to Tessie Du Motay and the Chemischen Fabrik Greisheim-Elektron, as will be pointed out in a more detailed manner in the following.

**Engels** \* has made a careful study of the reaction between carbon monoxide, water vapor and lime. The investigations show that the most suitable temperature lies between 450° to 550° C. Below 450° C. the reaction progresses too slowly, while above 550° C. the conversion does not go to completion or side reactions occur. Engels studied the effect of additions of an oxide, such as iron oxide, to the lime in order to catalytically hasten the reaction and found its course to be much improved by the addition of a few per cent of such catalyzer. The reaction is exothermic so no further external heating is necessary after the conversion has begun.

In 1880 **Tessie du Motay** devised a process for the production of hydrogen from water gas.† The latter gas mixed with steam is

\* Über die Wasserstoffgewinnung aus Kohlenoxyd und Kalkhydrat. Dissertation, Karlsruhe, 1911.

† U. S. Patents 229,338, 229,339 and 229,340, June 29, 1880.

passed into a converter containing lime where hydrogen and calcium carbonate are formed. Fig. 57 shows a plan view of the apparatus, in which *A* is a water-gas generator, *B* represents purifiers in which

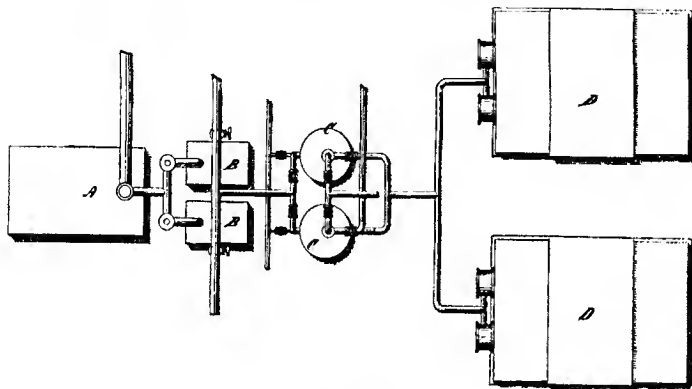
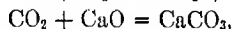
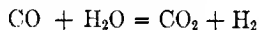


FIG. 57.

sulfur is removed, *C* designates superheaters where steam is mixed with the water gas. The preheated mixture then passes to a converter shown in Fig. 58. The inclined passageways of the latter are filled with lime in contact with which the reaction



progresses, yielding hydrogen gas. In lieu of water gas, coal gas or the vapor of naphtha may be similarly treated.

The process of the **Chem. Fabrik Greisheim-Elektron**, referred to above,\* involves mixing water gas with an excess of

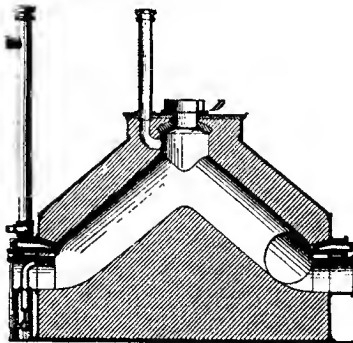
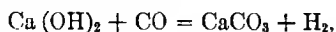


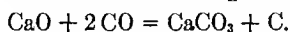
FIG. 58.

steam and passing this mixture over lime or hydrated lime to which about 5 per cent of iron powder has been added. The lime is heated to approximately 500° C. in an upright retort fitted with an agitator. The following reaction takes place:



\* Zeitsch. f. angew. Chem. (1912), 2401; British Patent 2523, Feb. 2, 1909.

with evolution of heat, and the reaction chamber is cooled so that the temperature does not exceed 500° C., or the temperature at which calcium carbonate commences to dissociate. The carbonate is regenerated by subsequent calcination.\* The presence of water vapor or of lime in the hydrated condition is essential for the reaction.† If absent or present in insufficient quantities the carbon monoxide is absorbed by the lime without the formation of hydrogen. In the absence of water the reaction runs according to the following equation:



According to the statement of Lepsius hydrogen of 97.5 per cent purity is obtained at a cost of about 2 to 2.5 cents per cubic meter.

The production of hydrogen by the action of carbon monoxide and steam on quicklime is regarded by **Levi and Piva** ‡ to be dependent on the intermediate formation of calcium formate.

**Merz and Weith** § have noted that when moist carbon monoxide is passed over soda lime heated to 300° C. or over, hydrogen is formed. A simple process for the production of hydrogen based on the observations of Merz and Weith has been put forward by the **Société générale des Nitrures in Paris**. A mixture of producer gas and water gas is treated in the usual way to remove carbon dioxide and is then passed over hot lime, which treatment yields a mixture of nitrogen and hydrogen free from carbon monoxide. The composition of the hydrogen-nitrogen mixture may be adjusted by using different proportions of the producer gas and water gas.||

Jerzmanowski ¶ makes a hydrogen-containing gas with apparatus shown in Fig. 59.

A kiln *B* filled with lime is raised to a high temperature by burning producer gas from the generator *A*. As soon as a sufficient heat is attained in *B*, an injector *H* blows into *B* steam and petroleum, which are decomposed chiefly into hydrogen and carbonic acid along with small quantities of carbonic oxide, marsh gas and other impurities. The gases pass through a cooler *C* to the gasometer *D*, and thence to purifiers.\*\*

\* The Chemische Fabrik Griesheim-Elektron (British Patent 13,049, June 3, 1912) mix steam with gas containing carbon monoxide and pass the mixture upwards through towers packed with pieces of lime and heated to between 400° and 700° C. The lime, when exhausted owing to conversion into calcium carbonate, can be regenerated in situ by diverting the stream of gases and recalcining.

† U. S. Patent 989,955, April 18, 1911, to Ellenberger, assigned to the Chemische Fabrik Griesheim-Elektron, discusses these reactions.

‡ J. S. C. I., 1914, 310.

§ Ber. (1880), 719. See also Ber. 1880, 31.

|| Sander, *Zeitsch f. angew. Chem* (1912), 2406.

¶ J. S. C. I., 1884, 560.

\*\* The New York Oxygen Company produce hydrogen by heating together anthracite and slaked lime. On passing an excess of steam over the residuc in the retorts the reverse action sets in and the slaked lime is reproduced. This sequence may be continued many times without renewing the materials. (J. S. C. I., 1887, 92.)

By another process steam is allowed to act on carbon or carbonaceous matter to which both an alkali compound and lime have been added, the effect of the additions according to Dieffenbach and Moldenhauer (British Patent 8734, April 11, 1910) being to lower the temperature of decomposition and to give hydrogen free from compounds of carbon and oxygen. For example, 100 kilos of charcoal or coke, impregnated with a 10 per cent solution of potassium carbonate, are mixed with 500 kilos of quicklime, and the mixture is decomposed by steam at 550° to 750° C.

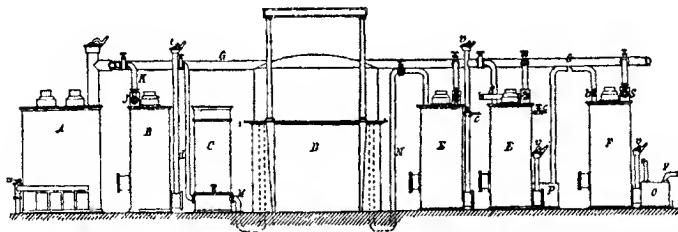


FIG. 59.

They also claim (British Patent 7718, March 30, 1910) the employment of other alkali compounds — such as chlorides and sulfates — for the same purpose. The fuel is impregnated with a solution of the alkali compound and dried, or, if practical, the fuel is coked after the addition of such compound. A comparatively small amount of oxygen may be introduced along with the steam for the purpose of maintaining the required temperature inside the decomposition apparatus. Granulated coal or coke may be treated with a solution of an alkali silicate or carbonate and the mixture briquetted and subjected to the action of superheated steam at temperatures from 550° to 750° C.\*

**Hembert and Henry** † pass superheated steam in a fine spray over coke heated to redness, whereby a mixture of hydrogen and carbon monoxide is formed. This mixture is led into a second retort filled with fireproof materials, also heated to redness. In the second retort steam is allowed to enter heated to its point of dissociation. These gases act upon one another, hydrogen and carbon dioxide being formed. The carbon dioxide may be absorbed by milk of lime. In this way 3200 cubic meters hydrogen are said to be obtained from 1 ton of coke.

In the production of a mixture of hydrogen and carbon dioxide by the action of steam on carbonaceous substances or on water gas, Sauer (German Patent 224,862, May 9, 1907) proposes to use an excess of steam and to superheat this to such a degree that it suffices to maintain the proper reaction temperature, in order to ensure the production of a gas of uniform composition. For example in the action of steam on coal, the latter is not blown alternately with air and steam, but the

\* French Patent 417,929, April 25, 1910.

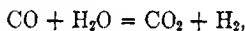
† Compt. Rend. (1885), 101, 797.

steam is superheated to such a degree that when the process is once started it is supposedly carried on continuously by aid of the heat of the steam alone.\*

For treating hydrogen and carbon compounds to oxidize the carbon to carbonic acid, in which form it may be readily eliminated, leaving pure hydrogen, **Moore** † brings the hydrogen and carbon compounds in a suitably divided state (generally as a gas or fine spray) into contact with heated oxide of iron, manganese, copper, tin, lead or zinc, in the presence of a jet of superheated steam. During the operation the oxides are said to be alternately reduced and reoxidized, acting as carriers of oxygen between the steam and the carbon compounds, so that the carbon present is converted into carbon dioxide, and leaves the chamber in which this is effected mixed with the hydrogen originally present and that resulting from the decomposition of the steam. The carbon dioxide may be removed by any known method, such as absorption by lime, or by water under pressure, or by a solution of alkaline carbonate.

**Mond and Langer** (British Patent 12,608, Sept. 1, 1888) bring carbonic oxide or gaseous hydrocarbons into contact with metallic nickel at a temperature of 350° to 400° C., or with metallic cobalt at 400° to 450° C., when decomposition takes place into carbon and carbonic acid or hydrogen, the carbon combining with the metal. If now steam, at a moderate temperature, be introduced this carbon combines with oxygen to produce carbonic acid, with simultaneous formation of free hydrogen. These various reactions take place simultaneously when the steam is passed through the apparatus along with the carbonic oxide or hydrocarbon, the ultimate products being carbonic acid and hydrogen. The former can be eliminated by any suitable means, such as by washing with milk of lime. The cobalt or nickel surfaces may be obtained by impregnating pumice stone with a solution of the metal, and reducing.

Similarly **Elworthy** ‡ heats a mixture of water gas and steam in the presence of such metals as nickel or iron to a sufficiently high temperature to induce the reaction,



whereby the hydrogen originally present in the water gas is increased by a volume equal to that of the carbon monoxide contained in it. The resulting carbon dioxide is removed by absorption by water under pressure, or by alkalis, or by other known means.

**Ellis and Eldred** § generate a hydrogen-containing gas as follows:

\* **Green** (British Patent 13,510, July 13, 1895) states he obtains hydrogen from water by an improved process, "which consists in burning steam with hydrogen gas, or with carburetted hydrogen, or carbon monoxide within a suitable chamber."

† J. S. C. I., 1885, 450.

‡ French Patent 355,324, June 17, 1905.

§ U. S. Patent 854,157, May 21, 1907.

Producer gas, generated by blowing air through a producer charged with fuel, is led through a superheating chamber filled with checkerwork of refractory material. The gas is then passed under a boiler and burned to generate steam. Water gas is mixed with steam and passed through the superheater to convert the carbon monoxide into dioxide. The mixture of carbon dioxide and hydrogen is then compressed; the former is separated in the liquid condition and the latter is collected separately. The process is rendered continuous by repeating the above steps alternately.\*

The essential feature of a process devised by **Dieffenbach** and **Moldenhauer**† is that a mixture of steam with a hydrocarbon or other suitable organic compound is heated to the temperature of reaction, or kept in contact with a catalytic body for only a short time and is then suddenly cooled or removed from the catalyzer, in order that the carbon dioxide formed shall have little or no opportunity for being reduced to carbon monoxide. From the resulting mixture of hydrogen and carbon dioxide, the latter can easily be removed, leaving more or less pure hydrogen. A suitable way of carrying out the process is to use as catalyzer wire gauze of nickel, cobalt, platinum, etc., disposed transversely to the direction of flow of the gases, and heated electrically to the requisite temperature. Instead of using external heating, the required temperature may be attained partly or entirely by combustion of a portion of the hydrocarbon by means of admixed oxygen.

**Naher** and **Muller**‡ prepare water gas by blowing superheated steam into a generator filled with coke, which has been heated to about 1000° C., and exhausted, and the gas produced, mixed with superheated steam, is passed over a contact mass of rhodium- or palladium-asbestos at 800° C. The resulting hydrogen then is freed from the accompanying carbon dioxide.

Carbon monoxide and steam are caused to interact at 300° to 600° C. under a pressure of 4 to 40 atmospheres in the presence of a catalyst, such as iron, nickel, or the like, with the production of carbon dioxide and hydrogen, the former being removed by absorption according to a process devised by the **Badische Company**.§

In order to better effect the reaction between carbon monoxide and water vapor in the presence of heated catalytic material and to carry on the operation continuously the **Badische Company** inject

\* Ellis and Eldred employ nickel, iron or manganese as catalytic material.

† German Patent 229,406, June 3, 1909.

‡ German Patent 237,283, Sept. 30, 1910.

§ British Patent 26,770, Nov. 21, 1912.

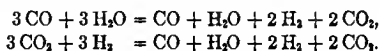


oxygen or air into the reaction chamber thus securing the necessary heating effect.\*

Pullman and Elworthy † generate a mixture of hydrogen and carbon dioxide by passing superheated steam in excess over red-hot coke or charcoal contained in a cast-iron retort, and the mixed gases after cooling are led through a number of porous pipes made of plaster of Paris or unglazed earthenware where they are separated to a great extent by diffusion, the hydrogen passing more rapidly through the porous walls of the pipes than the carbon dioxide.

After leaving the diffusing apparatus the nearly pure hydrogen is compressed into suitable vessels partially filled with water to absorb most of the remaining carbon dioxide. On opening the valves of the vessels the hydrogen rapidly escapes, and may be collected in a suitable holder and then given a final purification, either by washing with water in a scrubber or by passing it over some absorbent for carbonic acid, such as damp hydrate of lime, or through milk of lime. Instead of separating the mixed gases by diffusion, they may be taken from the cooling apparatus direct and compressed in strong metal vessels partially filled with water. The carbonic acid being much the more soluble, on opening the vessels hydrogen at first escapes rapidly and may be collected, the carbonic acid being afterwards collected in a separate receiver. The gases may be submitted to this operation several times over, and finally purified as above. Or instead of using water, glycerine or hydrocarbon oils which absorb more gas and part with it more slowly may be used.

That complete replacement of carbon monoxide by hydrogen in processes involving heating water gas and steam is impossible because of the conditions of equilibrium which obtain, is discussed by Gautier (Bull. Soc. Chim. (1906), 35, 929) who refers to the work of Boudouard (Bull. Soc. Chim. (1901), 25, 484). The latter determined the ratio  $\frac{\text{CO}}{\text{CO}_2}$ , in the equilibrium between carbon monoxide, steam, carbon dioxide, and hydrogen at different temperatures; and Hahn (Z. Physik Chem. (1903), 42, 705; 44, 513; (1904), 48, 735) determined the coefficient  $K = \frac{\text{CO} \times \text{H}_2\text{O}}{\text{CO}_2 \times \text{H}_2}$ , at different temperatures. When a current of carbon monoxide mixed with a varying excess of steam is passed through a porcelain tube heated to 1200° to 1250° C., at the rate of about 1 liter of the mixed gases per hour, or when a dry mixture of equal volumes of carbon dioxide and hydrogen is similarly treated at 1300 degrees, the reaction proceeds until the volume of hydrogen is about double that of carbon monoxide. The reactions correspond with the equations:



Under these conditions, any mixture of carbon monoxide, steam, hydrogen and carbon dioxide tends towards the composition,  $\text{CO} + \text{H}_2\text{O} + 2 \text{ H}_2 + 2 \text{ CO}_2$ . Small quantities of formic acid, but no formaldehyde, are produced.

Additional matter by Gautier appears in Comptes rendus (1910), 150, 1564, considering the reaction particularly from the reverse standpoint, that is, the reduc-

\* British Patent 27,117, Nov. 25, 1912; Chem. Zeit. Rep. (1913), 696.

† British Patent 22,340, Dec. 21, 1891.

tion of carbon monoxide by hydrogen. The results show that by heating carbon monoxide in the presence of hydrogen, water is actually formed. The reduction begins approximately at 200° C. The maximum formation of water is between 1100° and 1200° C.\*

By a process of the **Badische Company**† water gas is passed with an excess of steam over heated finely-divided metals of the iron group, especially iron, cobalt and nickel, or their oxides, and the carbon dioxide formed is eliminated from the gaseous reaction product. The catalyst is best prepared by the addition of appropriate diluents or binding agents, organic or inorganic, which may be such as to give off gas on heating so as to increase the porosity. For example, dry precipitated ferrous carbonate may be made into a plastic mass with lime, water, potassium hydroxide and ferric nitrate, and the mixture dried and heated to 500° C. A reaction temperature of preferably not over 600° C. is maintained by adjusting the temperature of the gases before they enter the contact chamber.

**Bosch and Wild**‡ produce hydrogen by passing carbon monoxide and steam over a catalytic material consisting of nickel or cobalt or non-metallic refractory material, which may be moulded into porous blocks.

Temperature ranges of from about 400° to 600° C., may be used. Iron may be substituted for nickel and cobalt provided it is supported on an inert substance. Bosch and Wild have found that it is possible to carry out the reaction to good advantage by passing carbon monoxide and steam over a form of catalytic agent containing at least 30 per cent of finely-divided nickel and more than 70 per cent of non-metallic, indifferent, refractory and porous material, the catalytic agent being porous and shaped into the form of blocks, tubes, rods, or the like. It is stated that excellent results can be obtained by preparing an oxide, hydroxide or carbonate of nickel, either by precipitation from solutions of its salts, or by heating suitable salts, such for instance as the oxalate or nitrate, while avoiding too high a temperature, then moulding the resulting products and if necessary heating before introduction into the reaction furnace. The production of hydrogen by the aid of such catalytic agents can be carried out by adding an excess of steam to a gas containing carbon monoxide and then passing the mixture of gases over the catalytic agent and subsequently removing the carbon dioxide which has been formed. The action of the catalytic agent is very satisfactory at temperatures of about from 400° to 500° C., or even less down to 350° C., but temperatures above 650° C. should be avoided. It is advisable to keep both the catalytic agent and the gases free from substances such as sulphur and chlorine which have a deleterious action. The following illustrates the method of producing a catalytic agent and of producing hydrogen by its means. Prepare a nickel hydroxide paste by introducing 5 parts of 25 per cent milk of lime

\* Met. and Chem. Eng. (1911), 511.

† French Patent 459,918, July 2, 1913.

‡ U. S. Patents Nos. 1,113,096, Oct. 6, 1914; 1,113,097, Oct. 6, 1914; 1,115,776, Nov. 3, 1914.

into 7 parts of molten nickel nitrate, add 10 parts of precipitated green nickel oxide ( $\text{NiO}$ ), knead the whole well, mould into the shape of briquettes and heat up to  $500^{\circ}\text{C}$ . Then place the briquettes in a suitable furnace and pass through it a mixture of pure carbon monoxide with an excess of steam, while maintaining a temperature of about  $500^{\circ}\text{C}$ ., and then extract the carbon dioxide from the resulting gases.

A catalyzer containing cobalt is prepared as follows:

Mix together 10 parts of finely-divided cobalt oxide (prepared by raising cobalt nitrate to a red heat), 1 part of calcined magnesia, and 2 parts by volume of a 50 per cent magnesium nitrate solution. Press the mixture into small briquettes, dry and heat up to  $500^{\circ}\text{C}$ .

When using an iron catalyzer, the following formulas are recommended:

(1) Add a solution of 100 parts of calcined sodium carbonate in 500 parts of water to a solution of 250 parts of ferrous sulphate in 500 parts of water. Filter off the precipitate and wash it, and then, without drying, mix it with 5 parts of slaked lime and dry until a paste is obtained which is then kneaded, rolled out, cut into cubes, dried, and heated at about  $500^{\circ}\text{C}$ . Instead of slaked lime, an agent can be employed which decomposes upon being heated, such for instance as 14 parts of calcium nitrate, or a mixture of 14 parts of calcium nitrate and 6 parts of ammonium nitrate.

(2) Knead to a paste 10 parts of finely-divided iron oxide, such, for instance, as the crocus maris of commerce, and a solution of 4 parts of aluminum nitrate in 4 parts of water. Form this paste into pieces of the desired shape, which then dry and heat at  $400^{\circ}\text{C}$ . in a current of air. In this example, the aluminum nitrate solution can be replaced by, for instance, a solution of 3.5 parts of magnesium nitrate in 3.5 parts of water.

(3) Melt 40 parts of crystallized ferric nitrate at from  $50^{\circ}$  to  $60^{\circ}\text{C}$ . and stir in a mixture of 5 parts of caustic lime, 15 parts of water and 2 parts of caustic potash. Then mix this product with 50 parts of precipitate which has been obtained according to (1) and then dried, work the mixture in a kneading machine until a plastic mass is obtained, roll this out, cut it into cubes, dry it and heat at  $500^{\circ}\text{C}$ . Sometimes it is desirable to pass over it a current of air or of carbon dioxide.

(4) Heat and stir ferric nitrate at  $180^{\circ}\text{C}$ . until its nitric acid is almost completely driven off, pass the residue through the finest sieve and mix 10 parts of this with 1 part of calcined magnesia, moistening it with a solution of 1 part of potassium carbonate in 1.6 parts of water. Press the mass into briquettes, dry them and heat to about  $600^{\circ}\text{C}$ .

(5) Boil 2.5 parts of wheat starch with 15 parts of water until a stiff paste is obtained, stir in 1 part of potassium carbonate, add 20 parts of iron oxide obtained by carefully heating iron oxalate to a temperature not exceeding  $600^{\circ}\text{C}$ . Knead the whole until a plastic mass is obtained, form it into briquettes, dry it and heat at about  $600^{\circ}\text{C}$ . In this example, gum tragacanth, dextrine, or gum arabic, can be employed instead of the starch.

(6) Mix 9 parts of ferric oxide hydrate with 1 part or more, of ferric oxalate and then work up the mixture to a paste with a solution of 2.5 parts of calcium nitrate in 2 parts of water. Press the paste into suitable shapes and dry slowly in a current of air at about  $500^{\circ}\text{C}$ . Then pass a mixture of pure carbon monoxide with an excess of steam over the catalytic agent thus obtained, while maintaining a temperature of about  $500^{\circ}\text{C}$ .

(7) Pass a current of carbon monoxide mixed with steam over iron in a state of fine division which has been preferably moulded in a briquette press, at the

same time gradually heating the catalytic agent, but avoiding temperatures above 600° C.

(8) Mix ferric oxide hydrate with sufficient concentrated calcium nitrate solution to obtain a paste of suitable consistency, then bring this paste into suitable shapes and dry it in the contact furnace while gradually raising the temperature to about 500° C. Then pass a mixture of carbon monoxide and steam over the catalytic agent, while avoiding temperatures above 600° C. Even if the gases are passed rapidly through the reaction furnace, an almost complete conversion of the carbon monoxide into carbon dioxide takes place.

(9) Heat ferric nitrate to about 200° C. so as to convert it into the oxide. Moisten the latter with aluminum nitrate solution and then mould it into suitable shapes and heat it at about 400° C., until the nitrous gases are driven off. Then place the catalytic agent in the contact furnace and pass a mixture of carbon monoxide and steam through the furnace while avoiding temperatures above 600° C.\*

Contact masses prepared by saturating pumice with a solution of nickel or cobalt chloride and subsequently igniting,† are stated by the **Badische Co.**‡ not to be satisfactory in the production of hydrogen from carbon monoxide and steam. Good yields of hydrogen are obtained, however, by using contact masses prepared by impregnating suitable materials with relatively small quantities of solutions of nickel salts free from halogens and sulphur.

The **Badische Company** § obtains hydrogen by the catalytic double decomposition of carbon monoxide or gases containing carbon monoxide with steam, with the employment of nickel.

Ordinarily while using nickel contact material an undesired by-product || is formed. To prevent the formation of methane there may be employed mixed contact masses, consisting of an excess of iron or its oxides with the nickel or its oxides. Other elements or their compounds which have active properties, are added advantageously. The specified contact masses, even at low temperatures effect a rapid and extensive decomposition and are to be preferred to nickel because of their stability and slight sensitiveness to accidental increases in temperature and to impurities in the gas mixture. The contact mass is applied preferably in the form of porous pieces. A suitable mass is obtained by precipitating a solution of 40 parts iron nitrate, 5 parts nickel nitrate and 5 parts chromium nitrate (all free from chlorine), with potassium carbonate and thoroughly washing. The mass is then formed, dried, and a water-gas-steam mixture is conducted over it at 400° to 500°. The amount of nickel can be increased or diminished. In a modification the principal portion of the carbon monoxide can be removed with a suitable catalyzer at 500° to 600° and the gas, while still hot, is freed from hydrogen sulphide by passage over

\* A mixture of gases and steam containing carbon monoxide is conducted at an elevated temperature over contact masses which comprise at least 30 per cent of finely-divided metals of the iron group (iron, nickel or cobalt) deposited chemically from metal salt solutions and which are made up into porous bodies with the addition of organic diluents or binders; **Badische Co.**, Austrian Patent No. 72,430, Sept. 11, 1916.

† See French Patent No. 463,114, of 1913; J. S. C. I., 1914, 313.

‡ German Patent No. 297,258, Sept. 11, 1914. Addition to German Patent No. 292,615, S. C. I., 1917, 873.

§ German Patent, No. 282,849, Dec. 4, 1913; **Chem. Abs.** 1915, 2437.

|| Methane.

copper, or the like, and then, with the addition of steam, it is conducted over the new contact mass at 350° to 400°.\*

Metals of the iron group such as iron, cobalt and nickel, or their oxides or mixtures of these in the form of porous pieces, briquettes, cubes, rods, tubes, etc., are prepared with the aid of inorganic and organic diluents or binders by the **Badische Company**.† Substances may be added which, upon heating, generate gas or wholly volatilize. Even at 400° to 500° and lower the action of the contact masses is exceptionally good. A suitable contact mass may be prepared as follows: A solution of 250 parts ferrous sulphate in 500 parts water is precipitated by means of a solution of 100 parts calcined soda in 500 parts water. The precipitate is washed, compressed, and intimately mixed without previous drying with 5 parts of slaked lime and then dried to obtain a mass which can be kneaded. This mass is rolled out, cut into cubes, dried and heated to 500°. The **Badische Company**,§ also employ, as catalyst, spathic iron ore, or a hydroxide iron ore, which has not at any stage of the process been subjected to a temperature appreciably higher than 650°. The catalyst may be employed in the form of grains, or may be made into shaped pieces with the aid of binding agents, such as hydroxides or salts of iron, aluminum, etc. The presence of phosphorus, sulphur or silica is objectionable.

**Vignon** § converts the carbon monoxide of water gas into methane by the following method. Water gas is mixed with a determined quantity of steam and passed over quicklime heated to 350° to 1200° C. Below about 850° C. calcium carbonate, methane, and hydrogen are produced, while above this temperature the calcium carbonate is decomposed, and the resulting gas also contains carbon dioxide. Small quantities of other hydrocarbons, such as ethylene, are also formed.

In the method of **Bosch and Wild** || hydrogen is produced by removing part of the carbon monoxide from water gas and treating the residual gas with steam under a pressure of about 60 to 600 lb. per square inch while subjected to the action of a catalyzer. The hydrogen may immediately be used under its original pressure in making ammonia. More hydrogen is obtained and the reaction is accelerated by producing the hydrogen under high pressure.

**Bosch and Wild** ¶ state that the heat necessary to enable the reaction to be started and also to maintain the temperature for the reaction can be generated with great ease, by supplying oxygen to the gases when in contact with, or on their way to, the catalytic agent, the oxygen entering into combination with the combustible gases and providing the required heat. Instead of pure oxygen, air can be employed in those cases where the presence of nitrogen in admixture with the hydrogen is not objectionable, for instance when the hydrogen obtained is to be employed for the catalytic production of ammonia. When water gas or other gas containing hydrogen and carbon monoxide is employed, and the oxygen introduced combines with a

\* J. S. C. I., 1915, 716.

† German Patents No. 292,615, July 24, 1912 and 293,943, Feb. 11, 1913; Chem. Abs., 1918, 855.

‡ Chem. Abs., 1916, 98; J. S. C. I., 1915, 800; British Patent No. 16,494, July 10, 1914.

§ French Patent No. 469,907, June 2, 1913; Chem. Abs., 1915, 19.

|| U. S. Patent No. 1,157,669.

¶ U. S. Patent No. 1,200,805, 1916.

part of the hydrogen to form steam, the latter can again take part in the reaction, and consequently the amount of steam employed can be correspondingly reduced. The oxygen, or air, is supplied directly to the contact chamber at one or more places.

The process can be carried out either with pure carbon monoxide or with carbon monoxide which is more or less diluted with other gases, and it is of particular use when it is desired to free a mixture of gases, such, for instance, as water gas, from carbon monoxide, since the conversion of the carbon monoxide into carbon dioxide sets free hydrogen which mixes with the hydrogen of the water gas. It is then only necessary to remove the carbon dioxide and any excess of steam, in order to produce pure hydrogen.

This process is claimed to offer great advantages when gases are employed which contain relatively little carbon monoxide, because, in this case, the heat of reaction is small and the difficulties incidental to supplying heat from the outside are consequently much exaggerated. In this case, the supply of oxygen can be so regulated that, during the combustion, sufficient steam is formed to enable the whole of the carbon monoxide to be oxidized and consequently further addition of steam is not necessary.

The **Badische Company** \* describe a method of producing hydrogen in which contact masses are used containing activating substances, especially oxygen compounds of chromium, thorium, uranium, beryllium, antimony, and the like, or mixtures of these, in addition to the usual catalysts. With such contact masses the reaction is practically quantitative at a relatively low temperature. The contact mass during preparation or use should not be heated above 600° C. Small quantities of carbon monoxide may be readily removed from gaseous mixtures with the aid of the contact masses described.

According to a somewhat similar method of the **Badische Company** † a mixture of carbon monoxide and steam is passed over a mixture containing a catalytic agent and a body which promotes the activity of the catalytic agent. Suitable catalytic mixtures consist of iron, nickel, or cobalt or their oxides, mixed with oxygen compounds of chromium, thorium, uranium, beryllium, or antimony; iron mixed with less than its weight of nickel; iron oxide of low activity coated with finely-divided iron oxide prepared at a low temperature, or zinc, lead, copper, vanadium, manganese or titanium, together with a promoter. The contact masses may be in the form of powder, porous lumps, etc., and binders, carriers, etc., may be added. The production of hydrogen is preferably effected at temperatures not exceeding 600°. Any suitable gas mixtures may be used, and the bulk of the carbon monoxide may be first removed therefrom catalytically, or otherwise. Hydrogen sulphide may be previously removed by means of copper. The presence of chlorine, phosphorus, bromine, or silica in the catalytic mixture should be avoided. The following examples of the preparation of the catalytic mixtures are given: A mixed solution of ferric and chromium nitrates, with or without aluminum nitrate, is precipitated by ammonia and the hydroxides are filtered off and pressed into suitable shapes; a mixture of ferric nitrate, ammonia chromate, and thorium nitrate, is heated to give the oxides; a solution of ferric nitrate, nickel nitrate, and chromium nitrate is precipitated by

\* German Patent No. 279,582, June 24, 1913; J. S. C. I., 1915, 355.

† British, Patent No. 27,963, Dec. 4, 1913; Chem. Abs., 1916, 97.

potassium carbonate and the precipitate filtered, washed, shaped, and dried; fine meshed wire netting is treated with ferric nitrate solution, and heated to decompose the nitrates; chromium nitrate or acetate is precipitated by ammonia, the hydroxide is mixed with precipitated zinc oxide, shaped and dried; Beryllium oxide may also be used; a mixture of lead nitrate or lead acetate and uranium nitrate solution is precipitated with ammonia, the precipitate is filtered, made into lumps, and heated; copper and zirconium nitrate solution is precipitated by sodium carbonate or potassium carbonate, filtered, the alkali salt washed out partly or completely, and the product moulded and dried; mixtures of oxides of manganese and chromium, titanium and antimony, vanadium and chromium or chromium and thorium are also suitable; aluminum oxide, alkali carbonates, etc., may be added as binding agents or promoters; a solution containing cerium and chromium nitrates is precipitated with ammonia, the precipitate filtered off, partly dried, made into a paste, shaped, and dried; other rare-earth salts may replace the cerium nitrate.\*

Considerable progress has been made in the production of hydrogen from water gas by reaction between carbon monoxide and water vapor. A mixture of water gas and steam is passed over a contact material of iron oxide with oxide of chromium and thorium as activating agents. The reaction takes place at a relatively low temperature which favors the yield of hydrogen from the standpoint of temperature equilibrium. Carbon dioxide is removed by treatment under pressure with water. Any carbon monoxide is eliminated by a copper chloride solution. The purified gas contains about 2 per cent of nitrogen and traces of methane. The cost of manufacture is low, as regeneration of the heat due to reaction suffices for carrying on the process.†

Hydrogen is produced, according to the Badische Company, by passing a mixture of a hydrocarbon and steam over a nickel catalyst distributed on a refractory carrier. Gaseous, liquid or solid hydrocarbons may be used, or hydrocarbon mixtures, as coal gas. The nickel catalyzer may be prepared in various ways. In one case fragments of magnesium oxide are impregnated with nickel nitrate solution. In another case, nickel is deposited on the carrier by the decomposition of nickel carbonyl. Temperatures of 700° and higher are used. For example, methane, mixed with three to six volumes of steam, is passed over the catalyst at a temperature of 800° to 1000°.‡

Ellis § employs a method of making hydrogen involving the treatment of lime or lime-material with carbon monoxide, or gases containing carbon monoxide. For example, carbon monoxide is passed over hydrated lime or carbon monoxide mingled with steam is contacted with lime, the latter being heated to a temperature of 450° to 600° C.

The monoxide takes oxygen from the water vapor forming carbon dioxide and liberating hydrogen and the carbon monoxide combines with the lime to form calcium

\* See also German Patent No. 282,849; J. S. C. I., 1915, 717; first addition, dated June 15, 1914, to French Patent No. 459,918, July 2, 1913; Swiss Patent No. 71,803, Feb. 16, 1916; Chem. Abs., 1916, 1918; Norwegian Patent No. 26,689, Feb. 21, 1916; Chem. Abs., 1916, 1582; German Patent No. 284,176, May 2, 1914; Chem. Abs., 1915, 2803.

† Z. Kompr. f. Gase, 1914, 16, 187-191; Zeitsch. angew. Chem. Referat., 1915, 203.

‡ British Patent No. 12,978, June 4, 1913; see also U. S. Patent No. 1,128,804, to Mittasch and Schneider.

§ U. S. Patent No. 1,173,417.

carbonate. This action is accelerated by the presence of catalytic material such as iron oxide and manganese oxide. The reaction is exothermic and once the mass of lime has been brought to the reacting temperature, sufficient heat is developed for continuance of the operation without the aid of externally-applied heat. In fact cooling may sometimes be required as the reaction does not progress with as good yields when the temperature is much above 525° or 550° C. Another consideration is the use of an excess of steam which greatly improves the yield of hydrogen.

Four to five times as much water vapor by volume as carbon monoxide should be present in order to effect substantially complete conversion. Difficulties are experienced in treating lime with gases to insure satisfactory absorption of the carbon dioxide, and it is desirable to remove the carbon dioxide as fast as it is formed in order to prevent by mass action the repression of the reaction due to the accumulation of the carbon dioxide, in the gaseous atmosphere.

To carry out the conditions required for the reaction Ellis makes use of a treating apparatus comprising a series of superimposed conveyers.

These conveyers are connected by chutes so that the lime and contact material, entering the uppermost conveyer, feed downwardly conveyer by conveyer and finally discharge from the lowest section.

The gas or vapor mixture flows upwardly from section to section in contact with lime material which is constantly but slowly moved forward in a direction opposite to the flow of the gases or vapors and under these conditions the carbon monoxide unites with the oxygen of the water, forming carbon dioxide, which combines with the lime, thus removing the carbon dioxide, as such, from the scene of the reaction and enabling a further conversion of carbon monoxide into carbon dioxide, so that the gases discharging from the upper section of the conveyer may be practically pure hydrogen or hydrogen containing only a small measure of contaminating products.

The lime which is employed for the operation preferably is low in magnesia, as dolomite and other high magnesia limes are not as desirable for this purpose. The lime should be finely divided, which may be accomplished by grinding, or the lime may be introduced in the hydrated form as a dry powder. The addition of about 5 per cent of finely-divided iron or manganese oxide is desirable to accelerate the reaction. The iron or manganese oxide preferably is derived by precipitation as a hydrate from aqueous solution and washing and drying the product.

The resulting carbonated lime is removed by a conveyer and is passed through a rotary kiln which may be heated by a producer gas or a powdered coal flame, and the lime regenerated; care being taken to not overheat the iron or manganese oxide to such an extent that its amorphous condition is lost. The regenerated lime, especially if not overheated, may be used repeatedly.

In place of carbon monoxide or water gas, producer gas, or even the vapors of oil, may be mingled with steam and passed over the lime to effect decomposition, thereby liberating hydrogen both from the oil and the water, forming first carbon monoxide and then carbon dioxide which is absorbed by the lime.

In the process of **Siedler and Henke**,\* water gas or other gas rich in carbon monoxide is mixed with steam and the mixture passed over lumps of lime arranged in superimposed layers in a vertical tower and maintained at a temperature of 400° to 750° by heat initially supplied by the gas and by the heat of the reaction.

\* Chem. Abs., 1916, 1708; U. S. Patent No. 1,181,264.



Hydrogen is manufactured according to **Griesheim-Elektron** \* from carbon monoxide, steam and alkali or alkaline earth.

When gases containing carbon monoxide and steam are conducted over calcium hydrate or caustic soda at temperatures of 450° to 550° hydrogen is obtained. This reaction is favored materially by employing increased pressure and correspondingly increased temperatures. In the same period of time four times as much hydrogen can be secured as when operating at atmospheric pressure. Either steam or a mixture of steam and gases containing carbon monoxide is conducted over a mixture of alkali or alkaline earth and carbon, or a mixture of steam and carbon monoxide is conducted, at an increased pressure, over alkalies or alkaline earths. Pressures of 10 to 100 atmospheres and over are employed. If gases containing carbon monoxide are to be acted upon alone, good yields are secured at five atmospheres pressure. With the use of lime, a temperature of 600° to 800° is suitable, and with the use of barium hydrate and alkali, a materially lower temperature may be employed. Especial advantages are secured by conducting steam, under a pressure of ten atmospheres and more, over a mixture of lime and coal or charcoal, almost pure hydrogen being obtained. Since the thermal effect is strongly positive, generally the application of heat is not required in a sufficiently large apparatus.

A tower may be used in which a charge of coal and lime is placed. The coal serves both as a source of heat and for the decomposition of steam. When by air blowing, the charge has been brought to the desired temperature, the supply of air is discontinued, and water or steam is conducted, from above, over the mixture, at twenty atmospheres pressure. The burned lime is discharged from below, mixed with fresh coal, and returned to the process. Brown coal or charcoal is preferred since they react more quickly and at lower temperatures than hard coal and coke.

**Vignon** † describes a horizontal or slightly inclined rotary retort which is charged with coal, anthracite, or coke, and quicklime, and a mixture produced by the rotation of the retort. The mixture is heated to 900° to 1000° C. and water or steam passed in until the temperature falls to 700° C. The gas is withdrawn and air passed through to raise the temperature to 900°–1000° C. and to regenerate the lime.

**Buchanan** and **Maxted** ‡ prepare hydrogen by passing a mixture of carbon monoxide or gases containing carbon monoxide and steam over a catalyst consisting of an alkali ferrite which has been lixiviated so that a portion of the alkali is removed; the alkali ferrite may be prepared by roasting ferrie oxide, from burnt pyrites, with sodium carbonate. Another method of producing hydrogen by Buchanan and Maxted § depends on the interaction of carbon monoxide and steam in the presence of a catalyst consisting of or containing a

\* German Patent No. 284,816, March 14, 1914; J. S. C. I., 1915, 1092; Chem. Abs., 1916, 101.

† French Patent No. 477,083, May 25, 1914; J. S. C. I., 1916, 592.

‡ British Patent No. 6,476, March 14, 1914; J. S. C. I., 1915, 177; Chem. Abs., 1915, 2434.

§ British Patent No. 6,477, March 14, 1914; Chem. Abs., 1915, 2434; J. S. C. I., 1915, 552.

metallic couple; Fe-Cu or Fe-Ag couples are suitable. The catalyst may be made from lixivated alkali ferrite, by reducing the ferric oxide therein to the metallic state by hydrogen, moistening with a solution of copper nitrate, and finally heating, preferably in a current of reducing gas, or washing, to remove nitrates. Gases containing carbon monoxide may be used instead of carbon monoxide in a state of purity. The couple is heated to 500° C. while passing carbon monoxide and an excess of air over it.

## CHAPTER XXI

### LIQUEFACTION AND OTHER METHODS FOR THE REMOVAL OF CARBON MONOXIDE

As uncarburetted or blue water gas consists of approximately equal parts hydrogen and carbon monoxide with small amounts of other gases, much attention has been given to methods of eliminating the monoxide by solution, absorption and liquefaction. The cost of removal of the carbon monoxide by solvents such as cuprous chloride and the like appears to be too great for commercial application. As the monoxide is relatively easily liquefied by cold and pressure, while hydrogen is extremely resistant to liquefaction under like conditions, processes have been devised for removing carbon monoxide in this way. As a source of cheap hydrogen this method offers attractive possibilities to concerns requiring large amounts of the gas. For small plants the relatively high cost of installation renders the use of liquefaction processes less feasible.

The pioneer work connected with the development of the liquefaction system towards a commercial goal should be credited to C. E. Tripler, who apparently was the first to devise methods and apparatus for large scale liquefaction of air and other gases. In 1893 Tripler patented \* the method of condensation "of a current of gas by expansion of itself over the conduit through which it passes." On this idea is based the present systems of separating hydrogen and carbon monoxide through liquefaction of the latter.

The principle of liquefaction by compression with counter-current cooling is shown diagrammatically in Fig. 60. The reducing valve *R* is so arranged that on the side carrying the receiver *B* for the liquefied product a pressure of 20 atmospheres is maintained, while on the other side the pressure is held at 200 atmospheres. The operation is as follows. Air is drawn from *B* by the compressor *K*, passing through the outer concentric tube of the coil. After compression to 200 atmospheres the air enters the cooler *KG* where the heat generated by compression is absorbed. The cooled compressed air flows through the inner tube of the coil to the reducing valve *R* where it is released

\* British Patent 4210, 1893.

at 20 atmospheres. Circulation in this manner is kept up until the temperature is lowered to the point of liquefaction.

Nitrogen boils at  $-193$  degrees, carbon monoxide at  $-190$  degrees and carbon dioxide at  $-78$  degrees while hydrogen boils at  $-252$  degrees and may easily be retained in gaseous form at temperatures which convert the other components of water gas to liquids or solids.\*

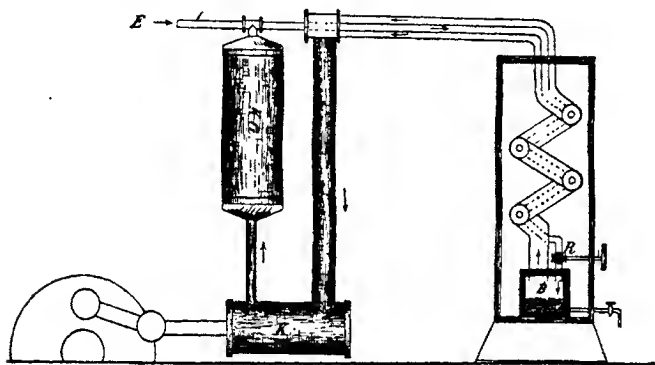


FIG. 60.

Apparatus in various forms has been devised by Linde,† Claude, Hildebrandt and others for the separation of the components of mixed gases by the liquefaction of the more easily liquefied constituents. The Hildebrandt system, shown in Fig. 61, consists of a coil of pipe of relatively large diameter through which two smaller pipes extend. The latter are indicated by 1 and 7 in the upper right-hand terminus of the large coil. Gas under the requisite high pressure enters at 1, passes along one of the small pipes within the larger pipe of the large coil, emerges at 2 and passes along the central riser to the expansion chamber *E*. Expansion with liquefaction occurs here. The liquefied product flows through 3 into the chamber *R* and from thence into a multiple evaporating coil 4, which consists of four coiled pipes having openings along their upper sides. Evaporation of the more easily boiling constituents takes place as the product flows downwardly along the evaporating conduits. The vaporized portion departs through the perforations of the coil and passes through 5 into the large pipe *A*, moving along this pipe as a current counter to the high-pressure gas entering at 1 and passing out of the system by the horizontal pipe shown on the upper right hand. The liquid fraction collecting in *G* flows along one of the narrow pipes to 2, thence through one of the narrow pipes in the large coil, upwardly and out at 7.

\* The production of hydrogen by liquefaction is clearly described by Linde in the Proceedings of the Third Int. Congress of Refrigeration, 1913. See also a very comprehensive treatise entitled, "Lowest Temperatures in Industry," issued by Gesellschaft für Lindes Eismaschinen, Munich.

† In a publication entitled "Lowest Temperatures in Industry," it is stated that five plants have been supplied by the Linde Co. for fat-hardening purposes and that

Linde makes note \* that Frank and Caro, with the aid of the Linde firm, have succeeded in the production of hydrogen of a high degree of purity from water gas. Figs. 62 and 63 show the apparatus diagrammatically.

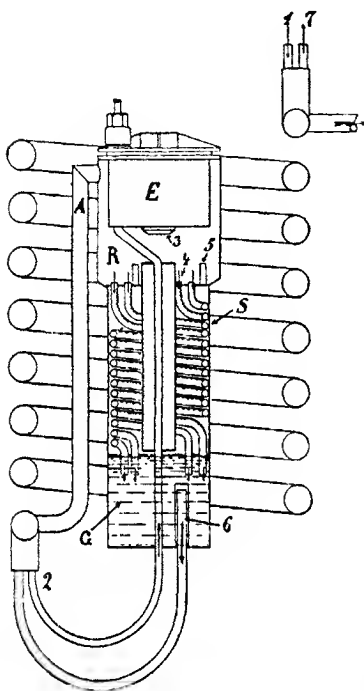


FIG. 61.

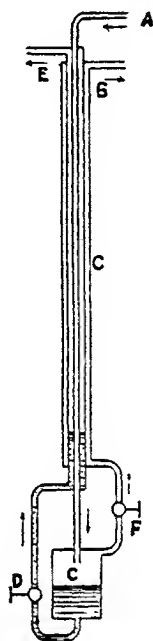


FIG. 62.

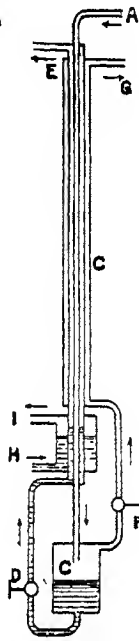


FIG. 63.

Compressed water gas enters by the innermost tube *A*, and is cooled by expansion through the valves and return of the cooled gases by the middle and outermost tubes *G* and *E* respectively, until liquefaction of the carbon monoxide occurs; separation then takes place, the gaseous hydrogen escaping through the valve *F* and the tube *G*, the liquid carbon monoxide passing through the valve *D* and evaporating

the total capacity of these is over 1000 cubic meters per hour. A plant in St. Petersburg uses 100 cubic meters; another in Nishnj-Nowgorod 30 cubic meters; Bremen-Bersigheimer Ölfabriken 200 cubic meters; United Soap Works, Ltd., Rotterdam, 200 cubic meters; and Ardol Co., Leeds, 500 cubic meters per hour.

\* J. S. C. I., 1911, 746.

in the middle tube. It was found impossible to liquefy the carbon monoxide, however, by the small amount of cooling by internal work of a gas containing so much hydrogen, and the cooling was therefore aided, as indicated in Fig. 63, by cold-jacketing the lower portion of the apparatus by means of a similar apparatus producing liquid air; in this way the industrial success of the apparatus was secured, and a gas produced, containing hydrogen, 97 per cent; carbon monoxide, 2 per cent; nitrogen, 1 per cent. Removal of the carbon monoxide by calcium carbide or soda lime then yields a 99 per cent hydrogen. The gas formed from the liquid contains 85 to 90 per cent of carbon monoxide, the rest being chiefly hydrogen, and is an excellent power gas.

By one process (Ges. für Linde's Eismaschinen A. G., French Patent 427,983, March 31, 1911) the strongly-cooled, compressed gaseous mixture containing hydrogen is passed through a heat interchanger so as to separate it into a gaseous portion, chiefly hydrogen, and a liquid portion, consisting mainly of impurities. The mixture passes into a receiver, which is provided with two separate systems for producing expansion; the liquid portion of the mixture collects in the receiver and is expanded in the lower system, from which it passes into the interchanger in the space surrounding the tube which conveys the original mixture into the receiver, and in the opposite direction to that of the gaseous current; the gaseous portion is expanded in the upper system and passed into the interchanger in the space surrounding the tube which conveys the mixture expanding from the lower system. From the interchanger the expanded hydrogen is collected free from impurities, which are thus condensed by the cold produced by the agency of the above-mentioned expansions. A supplementary refrigerating appliance, containing liquid air or liquid nitrogen, is used in conjunction with the apparatus for the preliminary cooling of the gaseous mixture.

A modified form of the foregoing consists in removing the portion of the gaseous mixture which is not liquefied, and comprises chiefly hydrogen, without allowing it to expand, the pressure remaining equal to that to which the compressed gaseous mixture has been brought. Liquid air or liquid nitrogen, used for refrigeration, is evaporated at a pressure below that of the atmosphere, in order to obtain a more complete separation of the remaining impurities. The liquid air or liquid nitrogen is thus used only for the ultimate refrigeration of the hydrogen which has already been freed from the main quantity of condensable gases. Also, the hydrogen, before it is brought to the expansion apparatus may be subjected to slight heating in a counter-current device, by means of the compressed gaseous mixture which has not yet been fractionated.\*

Frank † cools water gas in a suitable apparatus sufficiently to liquefy the carbon monoxide and dioxide, which are then separated. If the water gas has been produced at a low temperature, and contains

\* Ges. für Linde's Eismaschinen A. G., First Addition, to French Patent 427,983, March 31, 1911. See also U. S. Patents to Carl von Linde 1,020,102 and 1,020,103, March 12, 1912; 1,027,862 and 1,027,863, May 28, 1912; 727,650 and 728,173, May 12, 1903.

† British Patent 26,928, Nov. 27, 1906.

chiefly carbon dioxide, with but little carbon monoxide besides hydrogen, it may be completely liquefied, and the hydrogen recovered by fractional distillation. In either case the hydrogen resulting is further purified by being conducted over calcium carbide at a temperature of over  $300^{\circ}\text{C}$ .\*

The arrangement of a plant under the **Linde-Frank-Caro** system† is shown in Fig. 64. In this illustration *a* is a water-gas generator to

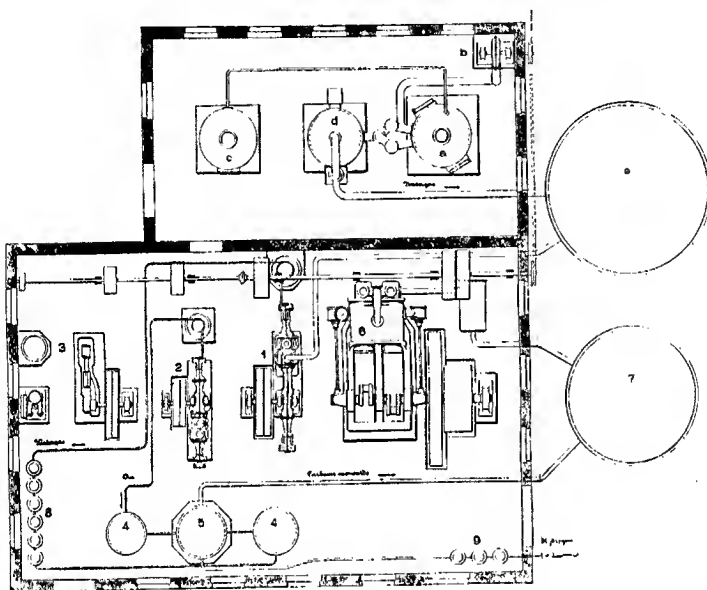


FIG. 64.

which air from the blower *b* and steam from the boiler *c* is alternately supplied. *d* is a scrubber and *e* a gasometer. 1 is a water-gas compressor, 2 an air compressor and 3 a refrigerating apparatus. For-coolers for drying the air and water gas are shown at 4. A water-gas separator indicated by 5 is also used for the liquefaction of air. A gas engine 6 operated by the rejected carbon monoxide (collected in gasometer 7) furnishes power for running the compressors. 8 represents

\* Frank (J. Gasbeleucht, June 10, 1911) has recommended (see J. S. C. I., 1911, 746) that apparatus for the production of pure hydrogen and other gases by cooling and liquefaction should be installed at gas works making water gas to enable hydrogen to be supplied on the large scale.

† Gesellschaft für Lindes Eismaschinen.

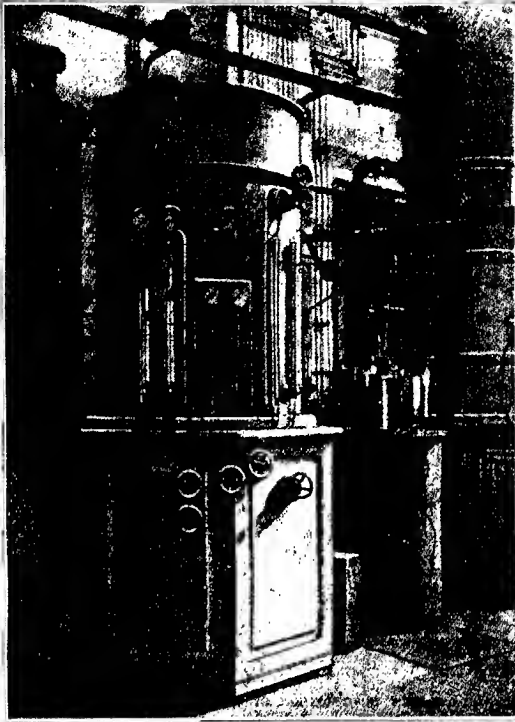


FIG. 65. Linde hydrogen apparatus.

purifiers for removal of carbon dioxide \* and 9 soda-lime purifiers for the ultimate purification of the hydrogen. Before purification by soda lime the gas consists of

	Per cent
Hydrogen .....	97-97.5
Carbon monoxide.....	1.7-2
Nitrogen.....	1.0-1.8

and after such treatment the composition is:

	Per Cent
Hydrogen.....	99.2-99.4
Nitrogen.....	0.6-0.8

An apparatus for separating hydrogen from the other constituents of water gas is shown in Fig. 66.†

\* The Bedford method of removing carbon dioxide by washing the gas under high pressure, with water, is used.

† Maschinenbau-Anstalt Humboldt, French Patent 445,883, July 8, 1912.





material capable of reacting to yield more or less pure hydrogen which is added to the water gas about to be treated.\*

Elworthy † separates carbon dioxide from a mixture of gases derived from water gas, containing hydrogen, carbon monoxide, methane, and carbon dioxide by simple compression of the cooled gaseous mixture, or by compression followed by expansion, when the carbon dioxide is liquefied or solidified, and can be removed. The gases escaping from the apparatus are utilized for cooling the incoming gases.

Jouve and Gautier ‡ propose to pass water gas through a porous partition, such as unglazed porcelain, in order to separate hydrogen by reason of its rapid power of diffusion. It is said that by one such operation the percentage of carbon monoxide may be reduced from 45 to 8 per cent.

According to Elsworth § water gas may be passed through a centrifugal gas separator, which is said to remove the bulk of the hydrogen, almost free from other gases.

Separation of hydrogen by an absorption method is recommended by Vignon. || Water gas, cooled and washed, is treated in a scrubber with an acid or alkaline solution of cuprous chloride, thus absorbing carbon monoxide; the hydrogen is thereby obtained free from carbon monoxide. The latter gas is recovered by heating the solution or subjecting it to reduced pressure, and the cuprous chloride is then used again. The carbon monoxide may be utilized by mixing it with air and burning it in the water-gas generator, so as to supply the heat necessary for the formation of the water gas, or this may be effected by burning the monoxide in a vertical shaft, filled with refractory material, fixed in the center of the generator.

Frank ¶ passes dry water gas over calcium carbide at a temperature above 300° C. Carbon monoxide reacts with the carbide forming calcium oxide, calcium carbonate and carbon, while the nitrogen present is converted into calcium cyanamide.\*\*

\* The Claude Company (Chem. Ztg. Rep. (1913), 521; French Patent 453,187, March 28, 1912) indicate that the present attainable yield (about 50 per cent) of hydrogen by the liquefaction system is increased and the loss through solution of hydrogen in carbon monoxide is diminished if the carbon monoxide gas carrying hydrogen is subjected to the action of hydrated lime to form calcium carbonate and hydrogen and the impure hydrogen thus secured is mixed with water gas and further treated in a similar manner.

† First Addition, June 16, 1906, to French Patent 355,324, June 17, 1905.

‡ French Patent 372,045, 1906.

§ British Patent 10,581, May 5, 1906.

|| French Patent 389,671, April 27, 1908.

¶ French Patent 371,814, 1906.

\*\* Thorpe Dict. App. Chem. III., 61.

Frank conducts water gas through milk of lime to remove carbon dioxide, then through cuprous chloride in hydrochloric acid solution to remove carbon monoxide and over heated calcium carbide to remove nitrogen as cyanamide. The carbide also removes traces of carbon monoxide and dioxide with separation of carbon in a finely-divided condition. The cuprous chloride solution is regenerated by exposing to reduced pressure to remove the monoxide.\* Subsequently Frank stated † that the expense of carbide, or of cuprous compounds or other means of absorbing carbon monoxide, was found to be too great and ultimately he was led to adopt the method of removal by liquefaction.‡

Claude § states that in the manufacture of hydrogen by partial liquefaction,|| hydrogen of 99 per cent purity can be obtained from purified water gas, but the process is open to objection that the maximum volume of hydrogen obtainable is equal only to one-half the volume of water gas employed.

In practice this yield is reduced owing to part of the hydrogen being held in solution in the carbon monoxide. Also an excessively minute adjustment at the exit cock for the liquefied carbon monoxide escaping from the liquefying apparatus is

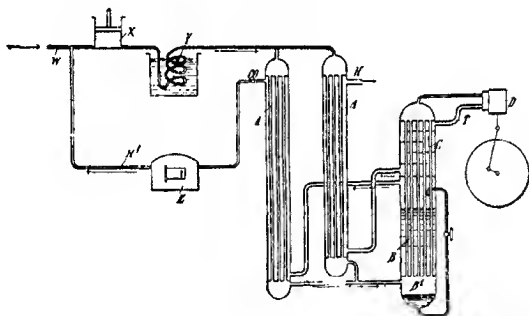


Fig. 66a.

required, but in practice this cock is generally opened wider than is proper. Claude recommends that the carbon monoxide separated from the water gas by partial liquefaction be subjected to chemical treatment to produce an approximately equal volume of hydrogen, this hydrogen to be added to further quantities of water gas

\* *Chemie der Gase*, Brahmner (1911), 97.

† *J. S. C. I.*, 1911, 746.

‡ See also Frank, U. S. Patent 873,853, Dec. 17, 1907.

§ U. S. Patent No. 1,135,355, April 13, 1915; French Patent No. 453,187; see also U. S. Patent No. 1,212,455, Jan. 16, 1917.

|| French Patent No. 329,839.

to be treated. He makes use of the reaction between carbon monoxide and heated calcium hydrate, affording a volume of hydrogen gas resulting from this step, which is approximately equal to the volume of carbon monoxide gas used. (See page 445.)

In carrying out the process of partial liquefaction, it is necessary to compress not merely the water gas but the mixture of water gas and the hydrogen obtained as an equivalent of the carbon monoxide; the ratio of the volumes of the gases in the two cases being about one to one and a half. The nitrogen that the water gas always contains in greater or smaller proportions accumulates slowly. As soon as this nitrogen attains too great a proportion, it should be removed.

The water gas to be treated passes through a pipe *W* (Fig. 66a) to the compressor *X* and thence to a cooling coil *Y*, when it passes to two temperature exchangers *AA*. From these exchangers the compressed and cooled water gas passes upward through the tubes of a carbon monoxide separator *BC*. The lower ends of the tubes are surrounded by the liquid carbon monoxide collected in a chamber *B'* under pressure and discharged into the part *B* under atmospheric or less pressure; the upper ends of the tubes are surrounded by the hydrogen resulting from the separation and expanded in an expansion engine *D*. The hydrogen circulated in the part *C* of the separator passes through one of the exchangers *A* and thence escapes by a pipe *H*, and the vaporized carbon monoxide from the part *B* of the separator passes through the other exchanger and escapes by a pipe *CO*. This carbon monoxide then passes into a chamber *E* where the reaction between the carbon monoxide and calcium hydrate takes place, and the resultant hydrogen passes to the pipe *W* to mix with the incoming water gas.\*

In a description of a process of *L'Air Liquide* † it is suggested that in order to obtain pure hydrogen by the partial liquefaction of water gas, the greater part of the carbon monoxide be liquefied by the cold produced by the expansion of the liquefied carbon monoxide from a previous charge. The last traces of carbon monoxide remaining with the hydrogen are liquefied either by the cold produced by the expansion of the whole or a portion of the separated compressed hydrogen, or by the evaporation of liquefied carbon monoxide containing dissolved hydrogen.‡

The **Badische Company** § have the following method of separating hydrogen from a gaseous mixture.

If water gas or similar gaseous mixture be compressed and then allowed to expand, the lowering of temperature produced is not sufficient to liquefy the constituents of the gas. The invention consists in adding carbon monoxide or nitrogen to the gas, before compression, in such proportion that the lowering of temperature produced on expansion is sufficient to liquefy the major portion or all of the constituents other than hydrogen. The enrichment of gas in carbon monoxide or nitrogen may be effected by modification of the method of preparation or by adding a suitable gas to the gaseous mixture containing hydrogen. When the process is once in operation it is only necessary to add a certain quantity of the constituents

\* See also French Patent No. 469,854, May 29, 1913; British Patent No. 13,160, 1913; Norwegian Patent No. 28,254, Oct. 8, 1917; Chem. Abs., 1918, 520.

† Soc. Anon. pour l'Etude et l'Exploit. des Proc. G. Claude.

‡ French Patents No. 457,297, Feb. 4, 1914, and 475,346, Feb. 10, 1914; J. S. C. I., 1916, 31.

§ German Patent No. 285,703, Feb. 18, 1913; J. S. C. I., 1915, 1133.

(carbon monoxide, nitrogen) which are liquefied, to the gas under treatment in order to obtain the desired results.

**Mewes** \* describes a process of liquefying and separating the constituents of air and like gaseous mixtures.

The **Linde** process for separating hydrogen from water gas by fractional liquefaction, the use of hydrogen in fat hardening and the manufacture of synthetic ammonia are discussed in *Seifenfabrikant*, 1914, 4.

\* British Patent No. 9,944, Apr. 28, 1913; *Chem. Abs.*, **8**, 1860.

## CHAPTER XXII

### HYDROGEN BY THE DECOMPOSITION OF HYDROCARBONS

When methane is heated to 1200° to 1300° C. dissociation occurs and lamp-black and hydrogen are produced. Acetylene is decomposed at a much lower temperature. In general, when subjected to sufficient heat hydrocarbons break down into their elements. This fact has been made use of for the production of hydrogen by decomposing various hydrocarbons and particularly heavy oils. Among the proposals put forward up to the present time are some which relate to the splitting of acetylene or natural gas by passage through the heat zone of an electric arc and separation of the hydrogen from the lamp-black or other carbonaceous material which is formed. The gas may be under pressure to render the decomposition more effective.

Pictet accomplishes this decomposition by treatment of the gas in heated tubes,\* as, for instance, an endothermic hydrocarbon, such as acetylene, is passed through a tube, the front portion of which is heated to about 500° C., at which temperature the gas dissociates into its elements with the evolution of a large quantity of heat. The latter raises the temperature of the tube sufficiently to dissociate fresh quantities of acetylene without the further application of external heat. The rear portion of the tube is surrounded by a refrigerating appliance, and the products of decomposition, hydrogen and lamp-black, are passed into a suitable apparatus for their separation. In the same way exothermic hydrocarbons, such as petroleum vapors, mixed with steam may be decomposed with the formation of hydrogen and carbon monoxide; in this case the combination of nascent carbon and oxygen supplies a portion of the heat required by the reaction, the balance which is required to dissociate steam and hydrocarbon being supplied by external heating. By admitting a regulated quantity of oxygen, the combination of the latter with nascent carbon may be made to provide all the heat required by the reaction, it being then only necessary to heat the hydrocarbons initially to their temperature of dissociation. The apparatus may conveniently consist of a steel, iron or porcelain tube, one portion of which is heated by means of a gas furnace, and the other cooled by water, or by a liquid hydrocarbon,

\* French Patent 421,838, Oct. 26, 1910.

the vapors of which are afterwards admitted to the tube for their dissociation. The tube is provided with the conduits necessary for the admission of the raw materials and for the withdrawal of the products of dissociation, these conduits being preferably composed of "pure iron" covered with nickel; the lamp-black is separated by washing or by means of filters.

In a modification of the foregoing Pictet (British Patent 14,703, June 21, 1911) operates in such a way that the carbon, instead of being deposited in the form of soot, is converted into carbon monoxide by interaction with water vapor. External

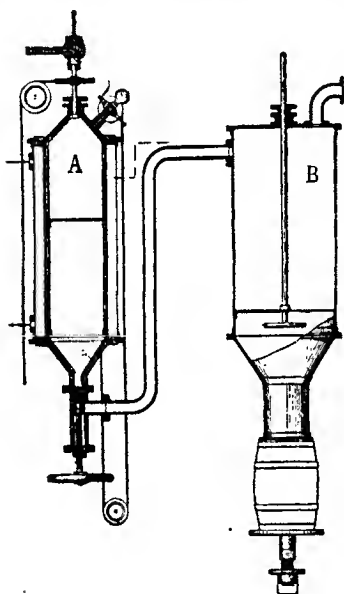
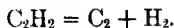


FIG. 67.

heat (39.36 units for every 18 grams of water) is applied for decomposing the water vapor, in addition to that required to decompose the hydrocarbon vapors, for which the temperature is raised substantially to the melting point of iron. Water and hydrocarbon are fed, for example, into an iron tube, which is of sufficient length (say 3 to 4 meters) to enable the supplementary heat to be imparted without damage, and these being vaporized on entry, react in the further end of the tube, which is the more strongly heated; the gas produced is then cooled and passes through a filter to a gas holder, there being a soot chamber and also arrangements for the removal of soot from the tube and filter. Ten liters of petroleum, mixed with 3 to 5.5 liters of water, may be thus decomposed per hour, in the apparatus described, the mixture furnishing approximately 3000 liters of gas for every liter of hydrocarbon, with a calorific value of 3000 to 3600 heat units per cubic meter. By regulating the supply of water, any desired proportion of carbon can be converted into carbon monoxide.

In preparing hydrogen from crude petroleum or petroleum tar oils (British Patent 13,397, June 3, 1911) the vapors are heated in such a manner that 18.1 calories are supplied to 16 grams of gas, with a tube temperature of 1200° to 1350° C.

Another process worked out by the **Carbonium Company** in Germany employs acetylene gas which is compressed to two atmospheres and exploded by an electric spark.\*



The acetylene thereby dissociates into the elements carbon and hydro-

\* Met. and Chem. Eng. (1911), 157.

gen. The carbon deposits in the form of lamp-black. The hydrogen is passed through large washer and stored. Its degree of purity is exceptionally high. For each cubic meter of hydrogen produced about one kilo of lamp-black is formed. A condition for getting the hydrogen cheaply by this method is that there is a market for the lamp-black.

**Wachtolf** \* compresses the acetylene to about 4 to 6 atmospheres and explodes electrically. In Fig. 67 the explosion chamber is shown on the left and a lamp-black collector on the right. The explosion chamber is provided with a rotary scraper to remove lamp-black adhering to the walls.†

**Geisenberger** ‡ generates hydrogen alone or mixed with carbon monoxide or carbon dioxide, by the action of heat alone or of heat and steam, on light hydrocarbons, such as benzine, or on other materials containing hydrogen and carbon, e.g., bitumen, shale, beeswax, turpentine, etc. The organic substance is heated in a retort, to which steam may be admitted, to its point of decomposition. The hydrogen is separated from the other gases in the mixture obtained, either by physical means, depending on the differences in density, or by chemical means, such as absorbing the carbon dioxide by means of sodium carbonate or hydroxide solution.

**Rincker and Wolter** § make use of two generators, somewhat resembling those used in making water gas, for the decomposition of oils and tars. These generators are arranged side by side and charged with coke. After they have been raised to incandescence by a blast of air, a charge of tar is introduced into one of them and is partly transformed into gas by the glowing fuel. The gas formed escapes by its own expansion. A current of air is then introduced which carries forward the remaining vapors of tar into the second generator where they are converted into a permanent gas. At the same time the blast of air raises the contents of the first generator to incandescence again, and the process is reversed by introducing the tar into the second generator and repeating the operations in the reverse direction.

In a modified form of the apparatus || the two generators are arranged one above the other and are charged with coke. The coke in the lower generator is ignited and then brought to incandescence by a blast of air which has been preheated by being caused to pass through a jacket surrounding the upper generator. The fuel in the latter is

\* German Patent 194,301.

† Decomposition of hydrocarbons under pressure is described by Bosch, German Patent 268,291, July 14, 1911; Chem. Zeit. Rep. (1914), 32.

‡ French Patent 361,492, Dec. 21, 1905.

§ French Patent 391,868, May 11, 1908.

|| French Patent 391,867, May 11, 1908.



also ignited and then raised to incandescence by natural draught. The products of combustion are allowed to escape to the chimney. When the fuel is glowing brightly, the air supply is cut off and a charge of oil is introduced into the lower generator through pipes in the top. The oil passes over the glowing fuel and is partially converted into permanent gas which escapes through a pipe in the side by its own

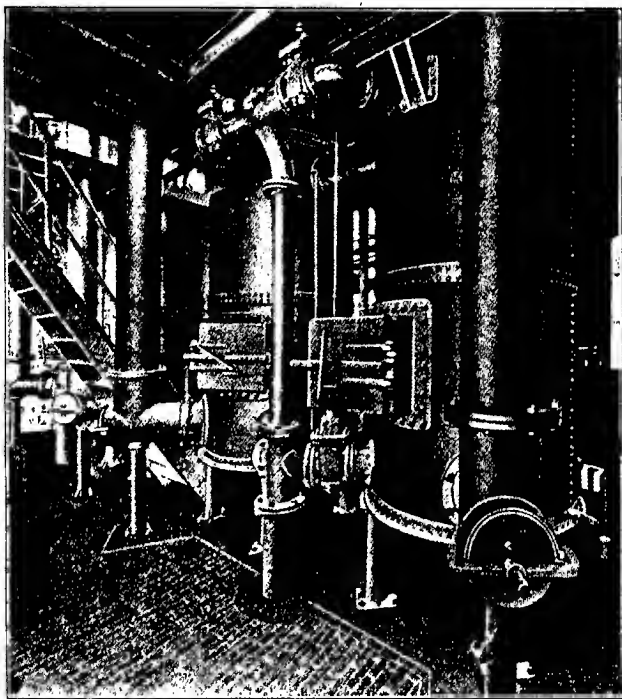


FIG. 68.

expansion. The blast of air is then again turned on, whereby the vapors of oil left in the lower generator are blown into the upper one, where they are gasified and fixed during their passage through the glowing fuel. The lower generator is at the same time again raised to incandescence and the process is repeated.\*

\* Apparatus for the production of hydrogen by the decomposition of the vapors of oil or tar by exposure to a high temperature is the basis of a patent to the Berlin-Anhaltische Maschinenbau-Aktien-Gesellschaft, Berlin, German Patent 267,944, Jan. 28, 1913; Chem. Zeit. Rep. (1914), 31.

Equipment for the Rüchker-Wolter system is manufactured by the *Hollandse Residugas-Maatschappij* of Rotterdam. The gas-making plant consists of twin generators, Fig. 68, lined with firebrick and provided with grate bars and clinkering doors, in short, resembling water-gas generators but lacking a carburettor and superheater. The generators are connected near the top and in the upper part are lids for feeding purposes, which carry sprayers for introduction of the oil.

Fig. 69 shows the operating floor of one of these plants. The generators are

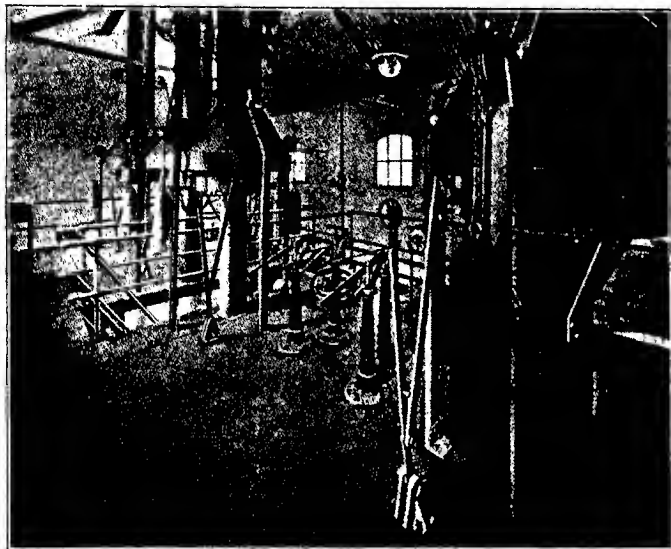


FIG. 69.

equipped with primary and secondary blast pipes, steam inlets and dust collectors. Both generators are charged with coke and fired. The generators are operated alternately in the blowing-run, the first generator receiving the primary, and the second generator the secondary, air blast. Combustion is incomplete in the first generator and the producer gas obtained is led to the second generator where it is burned on meeting the current of secondary air, thus heating up the second generator.

As it is preferable to reach nearly equal temperatures in both generators, the sequence is reversed after a short blowing and the first generator becomes second in the series. When both generators have reached the proper temperature, the air valves are shut and the gas run begins. The temperature of the fuel bed has to be varied somewhat according to the nature of the raw materials. For hydrogen production a temperature of about  $1200^{\circ}\text{C.}$  is required. Too low a temperature gives so impure a gas that subsequent purification of the hydrogen is rendered costly. At the end of the blowing-run oil is sprayed for several minutes on the hot coke and gasification takes place. Immediately after this the sprayer is cleaned by blowing steam through it. The gas formed by decomposition of the oil passes to a seal and from there to scrubbers and purifiers.

Fig. 70 shows the gas outlets and seal. The residue of gas in the generators is expelled by steam. Lamp-black is deposited in the generators and is consumed in the next run. Fig. 71 shows the generators of a plant at Utrecht.

In a well-handled run gas of the following composition is said to be obtained:

	Per cent.
H.....	96
N.....	1.3
CO.....	2.7

And by passing this gas over heated soda-lime a gas has been secured analyzing:

	Per cent.
H.....	98.4
N.....	1.2
CO *.....	0.4

To avoid difficulties from clinkering of the ash of the fuel, the author has suggested the addition of a small proportion of lime to the charge of coke, so as to flux the ash and thus to enable the maintenance of the requisite high temperature in the fuel bed.†

A method of preparing hydrogen is proposed by the *Badische Anilin und Soda Fabrik* ‡ according to which a mixture of hydrocarbons and steam is passed over an inactive, refractory oxide, such as magnesia, coated with nickel or nickel oxide, at a temperature of 800° to 1000°. The resulting gaseous mixture is freed from carbon monoxide and dioxide, leaving substantially pure hydrogen.

Efforts to secure hydrogen from illuminating gas have met with a considerable measure of success. By the process of *Oechelhauser* hydrogen of about 80 per cent purity is obtained. A gas of much higher hydrogen content has been produced by the *Berlin-Anhaltischen Maschinenbau - A.-G.* which is based on investigations made by *Bunte*. The illuminating gas is first freed of carbon dioxide and is then conducted over white-hot coke which decomposes the hydrocarbons and yields a gas mixture consisting almost entirely of hydrogen, carbon monoxide and nitrogen. The carbon monoxide is removed

\* Sanders (*Zeitsch. f. angew. Chem.* (1912), 2404) states that the cost of hydrogen by the Rinker-Wolter system is 10.5 to 14 pfennig per cubic meter. In a private communication to the author, the manufacturers advise the cost of the smallest equipment they make, having a capacity of 3500 cubic feet of hydrogen per hour, is \$2575 plus erecting expenses. With oil at about 4 cents per gallon the hydrogen is estimated to cost about \$1.75 per thousand cubic feet.

† Ellis, U. S. Patent, 1,092,903, April 14, 1914.

‡ J. S. C. I., 1914, 313.

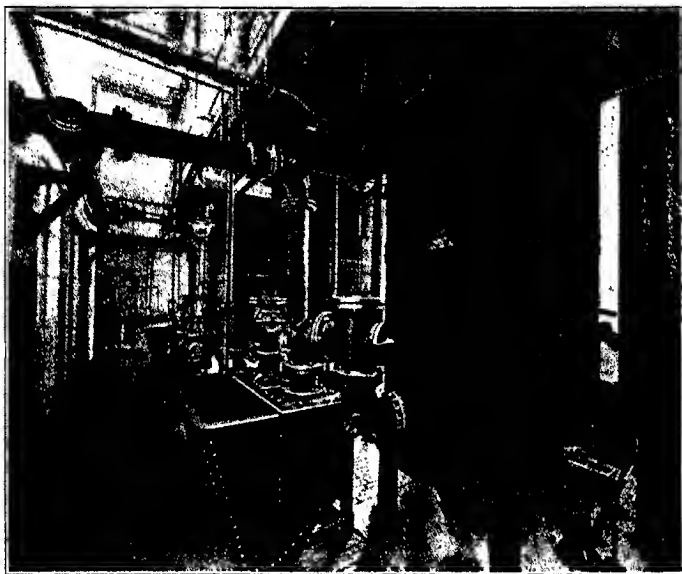


FIG. 70.

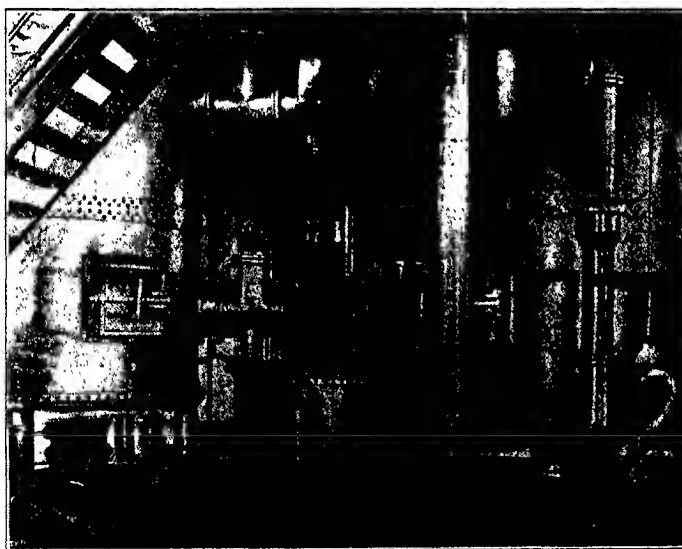


FIG. 71.

by treatment with soda lime and the gas then consists largely of hydrogen with only nitrogen as an impurity. The specific gravity is 0.085 to 0.097 and the gas has been found to be well adapted for most technical purposes. The process can be put in operation at any gas works equipped with a water-gas plant and the installation is not very costly.\*

**Pictet**,† in the production of a gas of high heating value, heats crude petroleum, tar oil or similar hydrocarbons in tubes to such a temperature (e.g., 900° to 1200°), that not all the hydrogen splits off as such, but appears in the end product as methane. The hydrocarbons to be broken down may be employed mixed with gases of less heat value, such as hydrogen, water gas, etc.

The addition of hydrogen and oxygen can be so proportioned that carbon monoxide and pure hydrogen alone result.‡ Pictet produces carbon monoxide and hydrogen § by simultaneously admitting steam, oxygen and petroleum oil (in vaporized

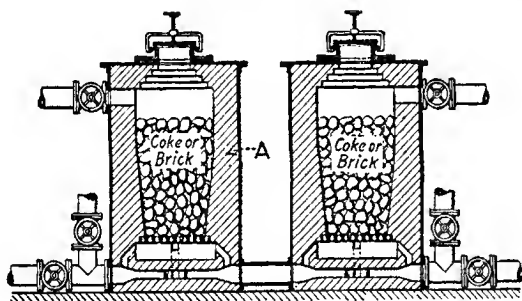


FIG. 71a.

form) into a horizontal pipe heated externally in a furnace to a temperature sufficiently high to decompose the steam and hydrocarbon. A temperature of 1300° to 1500° C. may be employed. A mixture of hydrogen and carbon monoxide is obtained.

**Frank**|| passes purified natural gas through a furnace filled with incandescent coke or refractory material thereby producing hydrogen. Natural gas is first freed of hydrogen sulphide by passage through a purifier which contains an iron oxide, such as limonite. Thereupon the gas is subjected to a temperature of at least 1200° C. The decomposition of the gas begins at a temperature of about 800° C., while the gas is completely split into carbon and hydrogen when the highest tempera-

\* Sander, *Zeitsch. f. angew. Chemie* (1912), 2406.

† German Patent No. 277,115, Feb. 13, 1913. Addition to No. 257,715; *Chem. Abs.*, 1915, 712; German Patent No. 289,065, Dec. 7, 1912. See also Canadian Patent, No. 184,460, May 21, 1918.

‡ U. S. Patent No. 1,134,416, Apr. 6, 1915; *Chem. Abs.*, 1915, 1374.

§ U. S. Patent No. 1,228,818, June 5, 1917.

|| U. S. Patent No. 1,107,926, Aug. 18, 1914; *Chem. Abs.*, 1914, 3359.

ture, exceeding 1200° C., is attained. Frank notes that at this temperature the higher hydrocarbons also are decomposed into carbon and hydrogen. The apparatus is shown in Fig. 71a.

**Rose \*** prepares gas containing as high as 98 per cent hydrogen by passing natural gas or oil over refractory surfaces heated to 1650° C.

The production of hydrogen and soot by the pyrogenic breaking down of light hydrocarbons, especially natural gas, by contact with highly-heated refractory surfaces, against which the gas under treatment is directed in a number of finely-divided currents is described by **Herman**.† With the exclusion of air, the baking and graphitizing of the soot on the surfaces may be prevented by a uniform heating of the surfaces serving for the decomposition and a careful removal of the soot from the heated surfaces after its formation. The hydrogen is drawn off and cooled immediately.

**Mittasch and Schneider ‡** pass hydrocarbons and steam over a nickel catalyzer distributed on a fireproof carrier at a temperature of somewhat above 700° C. and produce hydrogen and carbon monoxide or carbon dioxide.§

They state that the conversion of hydrocarbons and steam into hydrogen and carbon monoxide or carbon dioxide can be carried out rapidly and completely by employing a nickel catalytic agent distributed on a fireproof carrier and by working at a temperature above that of dark redness, that is to say above 700° C. Mittasch and Schneider observe that during the reaction it is possible that the nickel is converted into an oxide of nickel; or vice versa, it is also possible that the oxide or other compound, of nickel is reduced to the metallic form or to a compound containing carbon, so that it is equivalent whether metallic nickel or nickel oxide or other suitable nickel compound be taken at the commencement of the reaction. Such carriers are employed as do not react with nickel oxide under the conditions obtaining during the reaction, since the contact mass, it is claimed, then retains its activity even after being employed for a long time.

When working according to the present invention, a gas mixture free from or containing only small quantities of hydrocarbons results and after removal of the carbon monoxide and carbon dioxide gives rise to hydrogen which Mittasch and Schneider note is suitable for the catalytic production of ammonia, or for reducing fats.

The process is carried out in upright furnaces or tubes lined with fireproof material. The necessary heat can be applied internally, by burning hydrocarbons in the reaction space and this heating can be carried on before or during the actual production of hydrogen. It is particularly advantageous to pass alternately mixtures of hydrocarbon or other fuel and air, and hydrocarbon and steam, into the reaction space since by this means it is easy to maintain the requisite temperature. The heat contained in the gases leaving the reaction space can be used to preheat the gas

\* U. S. Patent No. 1,254,360, Jan. 22, 1918.

† German Patent No. 290,883, Oct. 23, 1914.

‡ U. S. Patent No. 1,128,804, Feb. 16, 1915.

§ See French Patent No. 463,114, of 1913; J. S. C. I., 1914, 313; also British Patent No. 12,978, June 4, 1913.

mixture about to enter the furnace. The gas mixture obtained, in so far as it contains carbon monoxide, if necessary after adding a further quantity of steam, can be passed over a contact agent, in order to convert the carbon monoxide into carbon dioxide.

The following procedure will serve to illustrate the process: Magnesia in the form of lumps is burnt at a high temperature. The lumps are soaked with a solution of nickel nitrate so that the magnesia contains from about 2 to 5 per cent of nickel, and then, after heating to decompose the nitrate, the product is placed in a contact furnace and a mixture containing methane and steam is passed over it at from 800° to 1000° C. The reaction takes place rapidly and the activity of the catalytic agent does not diminish. Another method of producing a catalyst of this character, recommended by Mittaseh and Schneider consists in precipitating metallic nickel on a carrier by the decomposition of nickel carbonyl.

Instead of gaseous hydrocarbons, either liquid or solid hydrocarbons can be used, in which case the latter are first vaporized or are injected directly into the reaction space, or the pipes leading to the reaction space. Further, mixtures containing hydrocarbons can be employed such as coal gas. The nickel also can be used in admixture with other metals or metallic oxides.

**Brownlee and Uhlinger\*** employ a method of obtaining carbon monoxide, hydrogen and nitrogen from the products of combustion of internal combustion engines.

Natural gas, coal gas, or other suitable gaseous, liquid or solid carbonaceous substance, is mixed with an amount of air not sufficient for complete combustion, and the mixture is exploded in the cylinder of an internal combustion engine. The mixture is so regulated that the proportion of air is such as to yield the largest practicable quantities of carbon monoxide and hydrogen. For example, if natural gas is used, a mixture of approximately 1 volume of gas to 6½ volumes of air is preferably employed with a compression before explosion of 70 to 80 lb. Under these conditions considerable power is produced and at the time good yields of carbon monoxide and hydrogen are obtained. The mixture of water vapor, carbon dioxide, carbon monoxide, hydrogen and nitrogen resulting after the combustion or explosion is cooled to remove the moisture, then compressed, and the carbon dioxide, carbon monoxide and nitrogen liquefied in turn, thus leaving hydrogen in the gaseous state, but highly compressed. Instead of compressing and liquefying the carbon dioxide, etc., after the removal of moisture by cooling, this gas may be absorbed with suitable absorbents, as calcium hydroxide, and the carbon monoxide may be withdrawn by ammoniacal cuprous chloride solution, leaving the nitrogen and hydrogen to be separated by compression and liquefaction of the nitrogen. In place of air, nearly pure oxygen may be used.† A mixture of equal volumes of natural gas and oxygen may be employed under a compression of 70 to 80 lb. From 1000 cu. ft. of Pennsylvania natural gas 1300 to 1350 cu. ft. of hydrogen will be obtained.

**Brownlee and Uhlinger‡** describe a process of producing hydrogen and carbon black which consists in passing hydrocarbons, at a pressure

\* U. S. Patent No. 1,107,581, Aug. 18, 1914.

† U. S. Patent No. 1,107,582.

‡ U. S. Patent No. 1,168,931, Jan. 18, 1916, No. 1,265,043, May 7, 1918 and 1,276,487, Aug. 20, 1918. See also 1,276,385 to McCourt and Ellis.

above atmospheric, over a highly heated mass of refractory material which is free from easily reducible metallic oxides. The refractory material is first heated to about  $1400^{\circ}\text{C}$ . and then gas or oil vapors passed in from the top. The carbon is collected in a chamber and removed as collected by means of a screw conveyer. The hydrogen is purified if necessary and passed into a gas heater. Any carbon which may be deposited on the refractory material will be burned off on reheating for further decomposition. Fig. 71b shows a diagram of the apparatus.

**Bacon, Brooks and Clark \*** have devised a process for obtaining carbon black, and practically pure hydrogen, by the decomposition of

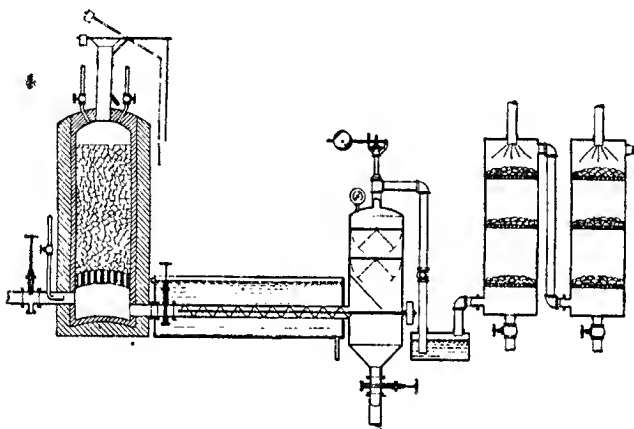


FIG. 71b.

hydrocarbons, the conditions of working being such as to insure a satisfactory yield of both products in a continuous operation. The apparatus employed is adapted to develop and maintain the high temperatures required and withstand, during long-continued use, the exacting requirements imposed upon it.

Bacon, Brooks and Clark state that unless the carbon black produced as one of the products of the decomposition is promptly removed from the high temperatures (exceeding  $1200^{\circ}\text{C}$ .) of the heating zone in which the decomposition is proceeding, such carbon black will deteriorate in quality for commercial uses, losing its desired deep black luster, and becoming materially duller and grayer. Accordingly, the operation is conducted so that the particles of carbon black will remain suspended in the hydrogen, and are removed with the hydrogen from the zone of decomposition.

\* U. S. Patent No. 1,220,391, Mar. 27, 1917. See also No. 1,276,385, issued Aug. 20, 1918, to McCourt and Ellis.



In Fig. 71c is shown a gas-tight metal shell, having a gas-tight cover. The casing is provided at one end with an exit pipe for the outflow of the carbon black and hydrogen, and has an opening at its opposite end closed by a removable gas tight asbestos board closure. Within the casing is a lining of fire-brick and an inner lining of magnesite brick. In the chamber is located the heating element which is made up of a double series of graphite rings cut in two diametrically. Through

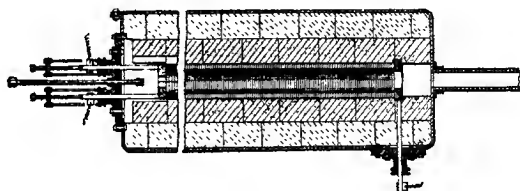


FIG. 71c.

stuffing boxes of the face plate there extend carbon rods, each of which is connected to the same terminal of an electric heating circuit. The hydrocarbon to be decomposed is supplied in a thin stream through the inlet pipe on the left. It enters the decomposition zone of the apparatus, made up of the annular walls of the series of graphite rings, which rings are heated by an electric current to a temperature exceeding  $1200^{\circ}\text{C}$ . and sufficient to flash and decompose the hydrocarbon into carbon black and hydrogen. The temperature of flashing or decomposition, and the quantity of liquid hydrocarbon injected are so adjusted that the gas pressure developed

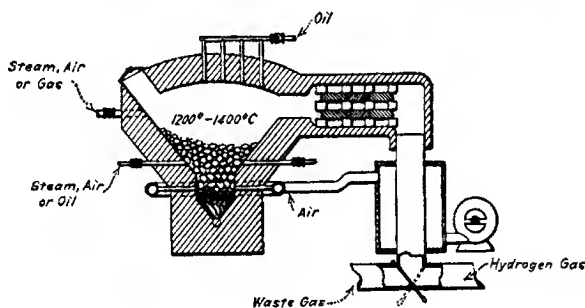


FIG. 71d.

shall be sufficient to sweep the particles of carbon black without permitting them to settle in the decomposition zone of the apparatus. The carbon black is deposited in a settling chamber, and the hydrogen is carried on to a gas holder. The carbon black recovered is of a black silky luster, and the hydrogen is substantially pure.

Ellis describes\* a type of furnace connected to a checker-work chamber, to be used for the heat decomposition of oils to yield hydrogen

\* U. S. Patent No. 1,092,903, Apr. 14, 1914.

A bed of coke in the furnace is heated to white heat and hydrocarbon oil entered above the bed where it is decomposed. The vapors pass through the heated checker work and are further decomposed. The furnace is provided with air and steam inlet pipes for blowing up the fire and for sweeping out contaminating gases. Fig. 71d shows this form of apparatus.

By a modification of the Rincker-Wolter process\* liquid hydrocarbons are converted into oil-gas, on contact with glowing coal or coke in the customary manner, and water gas or other gas containing hydrogen is led into the oil-gas generator with the object of converting the oil residues into hydrocarbons that can be gasified. The formation of tar in the oil-gas generator is thus avoided. Two generators are used, each serving as a water-gas generator and an oil-gas generator alternately.†

A portable plant of the Rincker-Wolter type, which may be used for military purposes, is arranged so compactly that it may be mounted on two ordinary railway flat cars. The apparatus consists of two gas producers in which hydrogen is made from oil which is sprayed into the producer. The gas is then passed through purifiers and driers to give hydrogen of the desired purity. In case it is necessary to compress the gas a third car is necessary.‡

Barth § produces hydrogen by first decomposing oil in a furnace and then further heating the gas formed in a separate furnace to produce hydrogen. He claims for this method that there is an economical use of fuel and that the contact mass in which the hydrogen is formed does not become contaminated with carbon, etc.

The furnace or vaporization chamber used by Barth, see Fig. 71e, is constructed of an iron jacket which has a lining of refractory bricks, and which is filled with a refractory grating or with coarse pieces of refractory material. The gases of combustion which escape from the generator during the blowing or reheating period are passed through the

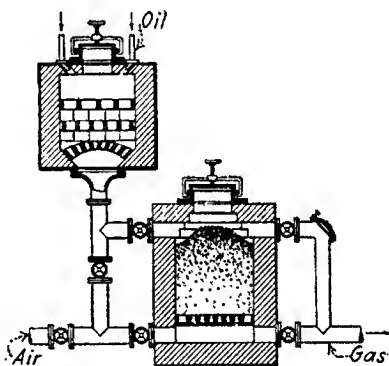


FIG. 71e.

\* British Patent No. 6,285, Apr. 27, 1915.

† See also Canadian Patent No. 181,962, Feb. 5, 1918.

‡ Scientific American Supp., Sept. 5, 1914, 155.

§ U. S. Patent No. 1,172,925, Feb. 22, 1916.

refractory grating of the vaporization chamber. Near the end of the blowing period the gases contain a certain amount of carbonic oxide which is burnt within the vaporization chamber by admitting air thereto. By this operation the grating of refractory material within the vaporization chamber accumulates the heat which is necessary for vaporizing the liquid fuel and in some cases for partly decomposing the same. Finally the air supply is shut off, and the vaporized oil or other fuel is passed into the vaporization chamber through several nozzles and vaporized therein. The vapors are passed through the glowing charge of coke within the generator, where they are decomposed in such a way as to split off carbon and to produce either an illuminating and heating gas (if the process is carried out at a temperature of about  $1000^{\circ}\text{C}.$ ), or hydrogen (if the process is carried out at a higher temperature). The vapors of oil or other fuel are alternately passed through the generator in opposite directions, that is alternately from above downward and from below upward. Thereby the heat which has been accumulated within the generator is uniformly consumed, and the lower part of the generator which, during the blowing period, is subject to the highest strain is not brought to an excessive temperature.

A process of producing hydrogen gas or gas containing this constituent is proposed by Lowe \* which involves heating a bed of solid fuel to incandescence, in passing into the ignited mass a quantity of petroleum oil which breaks down into hydrogen and carbon. The hydrogen is removed and the deposit of carbon is subjected to combustion with an amount of air sufficient only to consume part of the carbon which has been deposited. Then further quantities of petroleum oil are injected into the fuel mass.†

Snelling,‡ employs carbon compounds which are capable of dissociation by heat in a reversible manner, with the liberation of hydrogen. These compounds are heated in a closed chamber or tube with walls more permeable by hydrogen than by other substances present, and the hydrogen formed is thus withdrawn during the reaction.§

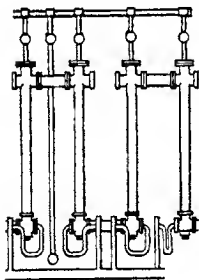


Fig. 71f.

An apparatus for producing hydrogen from natural gas, crude petroleum or garbage grease designed by Brunner|| employs a series of vertical stand pipes alternately connected at top and bottom and internally sprayed with water to remove carbon and other impurities. The water is finally discharged through a liquid seal at the bottom of each pipe. (See Fig. 71f.) The organic material is heated in an adjacent furnace (not shown).

\* U. S. Patent No. 1,174,511, March 7, 1916.

† See also Frasch, U. S. Patent No. 1,118,899, Nov. 24, 1914.

‡ J. S. C. I., 1915, 249; U. S. Patent No. 1,124,347, Jan. 12, 1915.

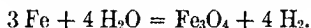
§ See also O. P. & D. Reporter, Apr. 5, 1915, 34.

|| U. S. Patent No. 1,246,867, Nov. 20, 1917; Chem. Abs., 1918, 297; J. S. C. I., 1918,

## CHAPTER XXIII

### HYDROGEN BY THE ACTION OF STEAM ON HEATED METALS

A large number of proposals for making hydrogen exist which are based on a very old reaction, namely, the passage of steam over red hot iron in a finely-divided state. The main reaction which occurs is



On the large scale it becomes necessary to regenerate the iron material; which is effected by reduction, usually with water gas. With an impure gas slagging difficulties arise. **Giffard** found that the charge of iron soon became inefficient because the sulfur in the gas formed on the iron particles a resistant coating of iron sulfide, which also acted as a flux and caused the iron material to sinter into a coherent mass. Hence prior purification of the reducing gas was found necessary for satisfactory operation. Apart from the sintering effect of sulfur on the iron material, the water gas should be freed from this element as otherwise the hydrogen would take up sulfur and poison the catalyzer. For each cubic foot of hydrogen produced, about three cubic feet of water gas are required. This requires the purification of three volumes of water gas for one volume of hydrogen.

Some of the processes described have had little or no commercial success, but are included because they involve certain features which are suggestive or instructive.

**Lewes** \* prepared hydrogen in the following manner:

A retort, partly filled with iron borings, or with a mixture of iron and carbonaceous material, or with asbestos containing iron in a very fine state of division, is placed in the center of a gas producer. By means of an air blast the fuel in the producer is raised to a bright red heat and then a little steam is admitted together with the air. The gaseous mixture of carbonic oxide, nitrogen and hydrogen produced in this way is led from the top of the producer down through the retort. As soon as the iron oxide in the retort is completely reduced, and the requisite temperature has been attained, the producer gas is turned off and steam, previously heated in the producer, is passed over the iron, the hydrogen being led away to a gasometer. The process is then repeated as described. One of the advantages claimed for this form of apparatus is that the rapid cooling of the iron during the decomposition of the steam is prevented. **Lewes** claims (British Patent 4134, March 7, 1891) the

\* British Patent 20,752, Dec. 19, 1890.

use of a mixture of carbonic oxide, nitrogen and hydrogen for the reduction of oxide of iron in the above process. This gaseous mixture is regarded as a better reducing agent than carbonic oxide, and is easily obtained. The finely-divided iron employed for the production of hydrogen is prepared by saturating asbestos or pumice with certain iron salts, which are easily decomposed into oxide of iron on heating, or by mixing moist hydrated oxide of iron with asbestos fiber and iron filings.

The **Dellwik-Fleischer Wassergas-Ges. m. b. H.\*** prepare iron by the reduction of a mineral oxide which retains both porosity and resistance after repeated use. In order to prevent deposition of carbon during the reduction of the iron oxide in the retort, the reducing gas is mixed with a volume of steam equal to at least half the sum of the carbon monoxide and hydrocarbons present in it. It is also found economical to carry the reduction only half way instead of completely to the metal, and this, moreover, gives purer hydrogen since no carbon can be deposited during such partial reduction. In British Patent 7849, of 1909, the Dellwik-Fleischer Co. make use of iron pyrites roasted to expel all sulfur and volatile metals.†

Hydrogen gas is produced according to **Hills and Lane ‡** by passing steam, preferably superheated, over iron contained in heated retorts; and the mixture of hydrogen and steam is led through coolers, from which the hydrogen passes to a gasometer. By means of reversing valves, controlling inlet and outlet passages, a reducing gas, such as water gas, coal gas or the like, is then led through the retorts to reduce the iron oxide formed, and then steam is again passed through. **Lane and Monteux §** secure the production of pure or nearly pure hydrogen in a continuous manner by the action of steam on red-hot iron. Finely-divided iron is contained in a series of vertical retorts, heated externally by gas, in combination with a regenerative system. The retorts are so connected that a current of steam passes through some, while the iron oxide, already formed, is being reduced in others by a stream of reducing gas sent in the opposite direction. Oxidation and reduction thus take place alternately, oxidation being found to occupy only half the time of reduction. The hydrogen produced is cooled and purified, to remove traces of carbon dioxide, etc. The reducing gas is made in a producer, and by introducing an excess of steam, it becomes rich in hydrogen. The excess of reducing gas is utilized for heating the retorts. After repeated use the iron becomes inactive, owing to an accumulation of impurities, but if these are burned away

\* French Patent 395,132, Oct. 10, 1908.

† British Patent 21,479, Oct. 10, 1908, and 7849, April 1, 1909.

‡ British Patent 10,356, May 7, 1903.

§ French Patent 386,991, Feb. 7, 1908.

by the occasional admission of air, the efficiency of the iron is said to be restored.

As it has been found in practice that the reducing reaction takes considerably longer than the generation of hydrogen, the Lane process (British Patent 17,591, July 29, 1909) may be carried out in three or more groups of retorts, the greater part of which are constantly subjected to the action of reducing gases for the regeneration of the iron, or other hydrogen-producing substance. The retorts communicate with one another by means of a series of pipes, fitted with controlling valves, so that steam or the reducing gases may be admitted as required. The hydrogen, which is evolved in the first few minutes of the operation, being impure, is diverted from the collector of pure hydrogen, and mixed with the water gas used for reduction. A considerable excess of water gas is used for reduction, and it undergoes a very thorough system of purification before being admitted to the retorts; the excess, which issues, is freed from the accompanying steam and used again. Means are provided for forcing hot air through the reaction chamber, which is done periodically between the two reactions so as to burn out objectionable impurities, especially sulfur. For the purification of the excess of water gas, or other reducing medium, which issues unchanged from the reducing retorts, the gas is passed into a cooler and washer, which removes mechanical impurities, and thence into a compressor. From the latter it passes under a pressure of several atmospheres into a strong receiver. The latter contains coke or the like material, down which cold water is distributed by means of a pump or other forcing device. The compressed gas, coming into contact with cold water, is freed from such impurities as sulfur dioxide, hydrogen sulfide, carbon dioxide, etc., either by solution or by condensation, being at the same time deprived of the greater part of its moisture.\*

With the Lane and similar apparatus it has been found † that the hydrogen gas obtained contains a relatively large proportion of gaseous and solid bodies or impurities, produced concurrently with the hydrogen and whose presence considerably increases the quantity of reducing gas necessary for carrying out the reduction operation, as well as the time necessary for effecting the deoxidation of the contact material. The presence of these impurities in the hydrogen gas is due to the fact that the reducing agent contains sulfur, carbon, etc., which either become deposited on the contact material or generate gases such as sulfurous acid, sulfuretted hydrogen or carbon dioxide. After the reduction phase a certain quantity of free reducing gas still remains in the retort, the presence of which contaminates the hydrogen and consequently lessens its commercial value.

Lane, therefore, proposes means for removing the reducing gas as well as the sulfur, carbon and other impurities between the two oxidizing and reducing steps of the process. To this end the retort is provided at each extremity with a multiple-way controlling valve adapted to establish communication between that end of the retort

\* Lane, British Patent 11,878, Jan. 29, 1910.

† Lane, U. S. Patent 1,028,366, June 4, 1912.]

and any one of three pipes connected respectively at the one end of the retort to a supply of air under pressure, a supply of reducing gas, and a hydrogen receiver, and at the opposite end of the retort respectively to an outlet, a gas-washing and regenerating apparatus, and a supply of steam under pressure.

In Fig. 72 *A* is the retort provided with an inlet *B* at the lower end and an outlet *C* at the upper end, and *F* and *G* are four-way valves which are capable of being rotated by means of hand-wheels *H* and *J* so as to open communication on the one

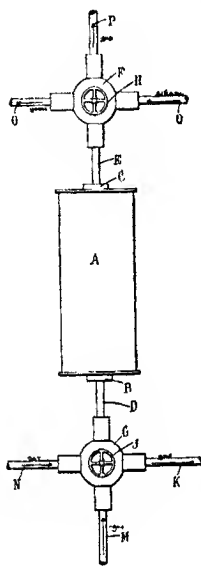


FIG. 72.

hand between the retort *A* and either the pipe *K* connected to a hydrogen container, a pipe *M* connected to a supply of reducing gas, or a pipe *N* connected to a supply of air under pressure, and on the other hand either with a discharge pipe *O*, a pipe *P* leading to a gas-washing or regenerating apparatus and a pipe *Q* connected to a supply of low-pressure steam. Assuming that the contact material in the retort has been oxidized during the previous hydrogen-producing phase, the sequence of operations is as follows. In the first place the impurities deposited on the contact material during the previous reduction phase, or present in the gaseous state in the retort, are removed by effecting their combustion. This is effected by rotating the valve *G* one-quarter of a revolution so as to admit air under pressure to the lower part of the retort through the pipes *N* and *D*, and rotating valve *F* so as to force out the products of combustion into the atmosphere through the pipes *E* and *O*. The valve *G* is then rotated so as to admit reducing gas to the retort through pipes *M* and *D* and rotating valve *F* so as to open communication between the upper part of the retort and the gas-washing or regenerating apparatus through pipes *E* and *P*. At the completion of the reducing phase the valve *F* is rotated so as to connect the upper part of the retort with the supply of steam under pressure through pipes *Q* and *E*, whereupon the pressure of the steam being greater

than that of the reducing gas remaining in the retort, the latter is forced out through pipes *D* and *M* carrying with it the impure hydrogen which has been generated by the action of the steam on the sulfur, carbon, etc., deposited on the contact material. As soon as it is found that the hydrogen passing out through pipe *M* is sufficiently pure the valve *G* is rotated so as to deliver the gas to the hydrogen container, after which, air is then again passed through the retort in the manner previously described.\*

\* Lanc (U. S. Patent 1,040,218, Oct. 1, 1912) purifies the reducing gas in the manufacture of hydrogen by the alternate oxidation and deoxidation of iron, by compressing the reducing gas to a pressure of several atmospheres and then causing it to flow (while still under pressure) in contact with an oppositely flowing stream of water. To increase the effectiveness of the washing operation, the gas is passed through a coke tower through which water is flowing in an opposite direction.

Fig. 73 shows the Lane system as installed in the works of a large soap manufacturer in England. Figs. 74 and 75 show the same system installed at a plant near Paris.

Lane states \* that in practice it has been found difficult to obtain pure hydrogen in consequence of the steam admitted to the retort during the oxidation state coming into contact with the reducing gas admitted during the previous reduction state and with the sulfur, carbon, etc., associated with and introduced into the retort by this



FIG. 73.

gas, the result of which contact being the formation of sulfuretted hydrogen, sulfurous acid, carbon dioxide, etc., and consequent contamination of hydrogen produced by the action of the steam. Lane proposes to remove the sulfur, carbon and other impurities left by the reduction phase, by admitting air under pressure to the retort and discharging the products of combustion into the atmosphere. The admission of air to the retort and the discharge of the products of combustion then ceases and reducing gas is admitted and passed through and out of the retort to a gas-washing and regenerating apparatus. When the reduction stage has been completed the admission of reducing gas is shut off and steam admitted. As a certain proportion of reducing gas will then be present, impure hydrogen will be produced and this is allowed to go to waste, until the product is found to be sufficiently pure. Thereupon the outlet to the atmosphere is closed and the hydrogen passed into a storage tank.

\* U. S. Patent 1,078,686, Nov. 18, 1913.



A process devised by **Messerschmitt** \* depends upon the alternate oxidation of spongy iron by means of steam, with the evolution of

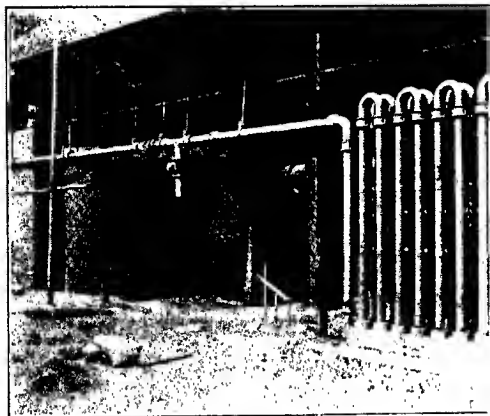


FIG. 74.

hydrogen, and the reduction of the resulting iron oxide † by means of reducing gases, such as water gas.

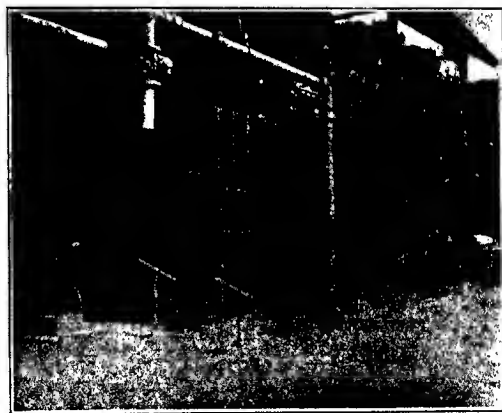


FIG. 75.

\* French Patent 444,105, May 22, 1912.

† After iron oxide has been used for a time it becomes partially or wholly inactive and has to be replaced by fresh material. It has been proposed to make the reducing chamber vertical with a grate at the bottom through which the spent oxide may be removed from time to time just as ashes are withdrawn from a gas producer.

An upright, cylindrical reaction chamber made of iron is suspended inside a furnace chamber, with which it is in open communication at the bottom, the lower end of the cylinder being provided with a grate to support the column of reacting material. The width of the reaction cylinder is relatively small, so that the contents may readily be heated from all sides, and the furnace chamber is provided with checkerwork constituting a superheater. Both the reaction cylinder and the furnace chamber are capable of being sealed, and are provided with a system of pipes and valves, enabling the introduction of either steam or water gas into the reaction cylinder or the furnace chamber. An air-supply pipe communicates with the furnace chamber, and a pipe leading from the top of the reaction cylinder can be put into communication with a gas purifier and the steam-raising plant. The process is carried out in three phases; water gas and air are first burned in the furnace chamber until the material inside the reaction cylinder has reached the required temperature. The air supply is then cut off and water gas, flowing in at the bottom of the furnace, becomes strongly heated, enters the open lower end of the cylinder, traverses the mass of iron oxide in an upward direction, and finally passes off at the top to the steam-raising plant, where any combustible gases are utilized. When the reduction of the iron oxide is complete the supply of water gas is cut off and steam is introduced, first into the bottom of the furnace to sweep out any residual gases from the second operation (the furnace being in direct communication with the chimney while this is going on), and then into the top of the furnace chamber, from which it passes downwards through the hot checker-work and finally upwards through the mass of spongy iron. Hydrogen issues from the top of the reaction cylinder and travels through a purifier into a gasometer. The iron receptacle may take the form of two concentric cylinders, the reaction material being in that case charged into the annular space between the two. The cylinders are periodically heated and reduced by means of the reducing gases, both inside and outside.

Messerschmitt has proposed to use compact iron (wrought iron or steel) as a support for spongy iron; only the surface layers of the compact iron taking part in the reaction. The spongy iron may, for example, be placed in the channels of a number of iron bars of U-shaped cross-section, or in perforated moulds, tubes, boxes or troughs of compact iron.\*

Elworthy † asserts that the various apparatus proposed for the production of hydrogen by the steam and iron method are subjected to serious drawbacks in practice, owing to the liability of the iron to cake together and to its difficulty of access and removal.

The iron rapidly cakes and chokes, so that the steam or gas comes into contact with only a small proportion of the active surface and loss of efficiency results. It is thus frequently necessary to remove and replenish the iron; but this is a troublesome operation, owing to the construction of the furnace and difficulty of the removal of the iron. Hence Elworthy places the iron in finely-divided form in a large number of separate trays of refractory fire-brick or the like, each adapted to contain a shallow layer of iron in finely-divided form and to be built up in successive layers from bottom to top of the furnace, so as to form a close-lying refractory

\* British Patent 12,117, May 22, 1912.

† U. S. Patent 778,182, Dec. 20, 1904.

filling (Fig. 76). The trays are open at their ends to enable the steam or gas to pass freely over them in contact with the iron when built up, and they have supporting flanges for supporting the under face of one tray at a suitable distance from the material on the tray below, and this under face of the tray radiates a quantity of heat onto the shallow layer of metallic iron during the heat-absorbing or oxidizing stage, while at the same time super-

heating the steam as it passes along the narrow shallow channel between the upper and lower series of trays. When the trays are built up in the furnace, they form a number of narrow flues containing a shallow layer of iron and running in a zigzag course from bottom to top of the furnace and affording free passage for the steam or reducing gas. These narrow flues, so to speak, divide up the mass of refractory material into a cellular structure such that the gases can pass freely through the cell flues over the iron.

Messerschmitt \* employs spongy iron produced from fragmentary oxide iron ore (i.e., an ore containing  $\text{Fe}_2\text{O}_3$ ). Only spongy iron produced from such oxidized iron ore is regarded by Messerschmitt as possessing the requisite porosity and strength for carrying out the process.

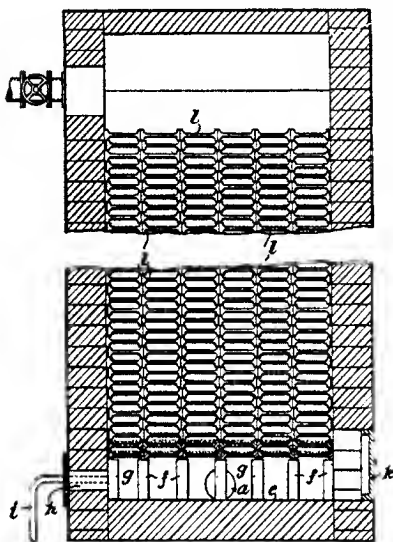


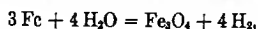
FIG. 76.

The effect of using ferrie oxide as raw material, it is claimed, is that the oxide after reduction becomes porous throughout its entire mass on account of the decrease in volume consequent upon the removal of the oxygen therefrom and thus an increased surface is exposed to the subsequent action of the steam. The use of ferrie oxide in the form of oxide ores is important because the lumps of this ore, in consequence of its peculiar natural texture, maintain their shape in spite of repeated reductions and oxidations and the ore possesses the necessary strength to withstand the pressure of superimposed layers; if this were otherwise the path for the gases would become choked by the crumbling of the ferrie oxide and continuous working would be impeded. The gangue, clay, silica and other components of the ore have for effect to prevent (in spite of high temperatures which may be produced either intentionally or in consequence of irregular working of the furnace) a sintering of the charge, the latter thus constituting a sort of rigid incombustible carrier for the oxides and the iron sponge.

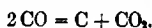
The presence of carbon monoxide in hydrogen gas-mixtures as at present produced by the action of steam on reduced iron is to be ascribed to the following: If ferrie oxide be reduced by means of carbon monoxide metallic iron and carbon dioxide are formed, but simultaneously a considerable quantity of carbon is precipitated from the carbon monoxide. Hence, if after completion of the reduction phase of

\* U. S. Patent 971,206 of Sept. 27, 1910.

the process, steam be led over the mixture containing spongy iron thereby produced, there is produced not only hydrogen according to the equation,

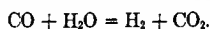


but also at the same time carbon monoxide and carbon dioxide resulting from the reaction of the steam on the carbon present, thus contaminating the hydrogen. Since the carbon present is incompletely decomposed by the steam at the comparatively low temperatures used, the carbon increases more and more by the repetition of the cycles (i.e., of the reduction and oxidation phases of the process) and consequently the impurity of the resulting hydrogen becomes greater and greater. From this the necessity of employing means for the prevention of the precipitation of carbon during the reduction phase will be evident. The precipitation of carbon from the heated carbon monoxide takes place, according to the equation,

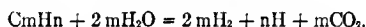


In order to prevent this precipitation of carbon the following method is used by Messerschmitt:

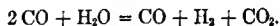
The gases destined for reduction and containing carbon monoxide and hydrocarbons are mixed with a quantity of steam such that the steam volume amounts, at the most, to half of the volume of the carbon monoxide plus that of the hydrocarbons. For reducing the ferric oxide (or  $\text{Fe}_3\text{O}_4$ ) this mixture may be directly led into the retorts or tubes containing the iron oxide without a considerable amount of carbon being precipitated. The reason of this result is explained as follows: If carbon monoxide be mixed with steam, hydrogen and carbon dioxide are formed and the volume of the first is the same as that of the carbon monoxide transformed into dioxide by the oxidation. In place of CO therefore an equal volume of  $\text{H}_2$  and an equal volume of  $\text{CO}_2$  is formed according to the equation,



In general the reaction with hydrocarbons is as follows:



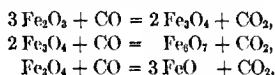
For every volume of hydrocarbon therefore one volume of  $\text{CO}_2$  and more than two volumes of hydrogen are formed. Now as only half of the carbon monoxide is oxidized by the steam to  $\text{CO}_2$  (since the amount of steam added is only half that of the CO) as final product a gas of the following composition is obtained according to the equation,



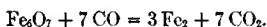
The gas used for reduction of the iron therefore would yield for every volume of carbon monoxide one volume of hydrogen and one volume of carbon dioxide, or for two volumes of reducing gases one volume of carbon dioxide. This proportion, however, should not be changed on account of the reducing gases because otherwise the reduction of the  $\text{Fe}_3\text{O}_4$  to metal no longer takes place. For this reason the addition of steam is restricted according to the above equation in order that the gas and steam mixture may be used directly for the reduction of the iron. This reducing gas of the composition  $\text{CO} + \text{H}_2 + \text{CO}_2$ , however, precipitates considerably less carbon during the reduction than pure carbon monoxide or carbon dioxide mixed with nitrogen (producer gas) would do. The reason for this lies in the presence of the hydrogen. The latter first attacks the ferric oxide with the formation of steam

which again reacts on the carbon monoxide and thus again produces hydrogen and carbon dioxide. By this means the carbon monoxide tending to precipitate carbon is continually reduced, whereas the carbon dioxide and the hydrogen (neither of which precipitates carbon) is increased. From this Messerschmitt concludes that the presence of hydrogen considerably restricts the precipitation of carbon from the carbon monoxide. Hence Messerschmitt proposes to provide for the addition of steam in such manner that its volume only amounts to about half of the combined volume of the carbon monoxide and that of the hydrocarbons contained in the gas.

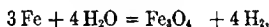
The reduction of ferric oxides to spongy iron by means of reducing gases takes place very gradually, the iron being gradually reduced to lower stages of oxidation according to the following equations,



from which combinations metallic iron is formed by a further reduction according to the equation,



A surplus of reducing gas is necessary in order to render the reduction to spongy iron complete. Since between the products of oxidation ( $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ) produced and the reducing gases ( $\text{CO}$ ,  $\text{H}$ ,  $\text{CnHm}$ ) a relationship of equal weights, according to Messerschmitt, subsists which is not affected even by prolonged reaction on the ore, the waste gas of the reduction always contains a considerable amount of reducing gases. The more unfavourable the proportion of undecomposed and decomposed gases in the waste gases becomes, the more difficult it is to reduce the ore. Reduction takes place easily at the beginning, whereas it becomes more difficult as the ore becomes poorer in oxygen and the further reduction to spongy iron has progressed. It is immaterial for the production of the hydrogen whether, during the reduction phase metallic iron or a lower stage of oxidation than that of black oxide of iron is produced, since Fe as well as  $\text{FeO}$  and  $\text{Fe}_3\text{O}_4$  for instance are oxidized to  $\text{Fe}_2\text{O}_3$  when acted on at incandescence by means of steam while giving off hydrogen according to the formula,

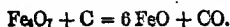


or



Now it has been found that the proportion of the gases necessary for the reduction relatively to the hydrogen produced during the oxidation phase remains relatively small and that efficient working is secured if the reduction of the ferric oxide ( $\text{Fe}_2\text{O}_3$ ) during the reduction phases is only incompletely effected (at most only half reduced).

By the reaction of the steam during the oxidation phase, several gases, methane, carbon dioxide and hydrocarbons, are formed from carbon iron combinations, contaminating the hydrogen. Absorption of carbon is impossible as long as (in addition to spongy iron) a surplus of oxides is contained in the ore. If, for instance, carbon were actually taken up it would of necessity have to be decomposed again by the oxygen of the oxide present, according to the equation,



A simple form of apparatus devised by Messerschmitt \* is shown in Fig. 77. The contact material in this case is iron in the form of tubes. These are shown at *d* in the furnace chamber *f*. The tubes *d* slip over the upright tubes *c* projecting from the top of the distributing chamber *b*. A filling of sand around the base of these tubes *d* seals them and yet allows their ready removal when replacement is required. The reducing gas is introduced by the inlet *a*.†

In another type of furnace for the production of hydrogen from reduced iron and steam, Messerschmitt ‡ makes use of apparatus as shown in Fig. 78. The reaction is carried out at different planes in this furnace. The walls are provided at different heights with heating channels *cc*. The gas and air nozzles 1, 2, 3 and 4 are so disposed

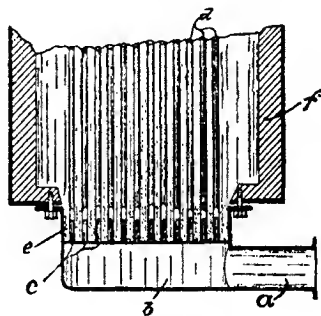


FIG. 77.

posed that the heating gases are discharged tangentially into the furnace in such a manner as to prevent local overheating of the iron. The oxidized iron in the different zones of the furnace is successively reduced and heated and the waste gases from one zone are burned by the aid of a blast of air in a higher zone. In the upper part of the structure the checkerwork *g* enables preheating of the reducing gas and steam.

Natural ores of manganese or of manganese and iron are employed by Messerschmitt § in place of ordinary iron ore. It is stated that hydrogen is obtained in good yields at 700° to 800° C. or about 200 degrees lower than with iron sponge.

\* Chem. Ztg. Rep. (1913), 521.

† A description of apparatus recently recommended by Messerschmitt appears in Chem. Zeit. Rep. (1913), 696. (German Patents 266,863, July 9, 1911, and 267,594, Feb. 9, 1912.) Messerschmitt has also taken out German Patent 268,339, Oct. 18, 1912, supplementing patent No. 267,594. (Chem. Zeit. Rep. (1914), 31.) A method for the manufacture of hydrogen by the alternate oxidation and reduction of iron is described by Messerschmitt in German Patent 268,062, Nov. 3, 1912. (Chem. Zeit. Rep. (1914), 22, and Zeitsch. f. angew. Chem. (1914), 47, No. 5; (1914), 61, No. 7.) See also German Patent 263,390, July 24, 1912.

‡ Chem. Zeit. Rep. (1913), 521; German Patent 263,391, July 26, 1912.

§ J. S. C. I., 1914, 201; French Patent 461,480, Aug. 19, 1913. Additional methods employed by Messerschmitt for the generation of hydrogen are described in J. S. C. I., 1914, 313.

An apparatus employed by the **Internationale Wasserstoff-Aktien-Gesellschaft** is shown in Fig. 79. On the left is a gas producer supplying fuel gas to heat the two vertical retorts shown on the right. The heating gases and products of combustion move in the direction indicated by the arrows and finally pass to an exit flue. The valves

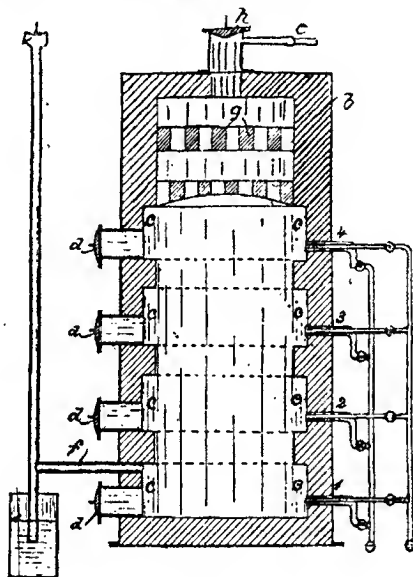


FIG. 78.

*a* and *b* are opened and water gas flows through the iron ore filling the retorts, reducing iron oxide to finely-divided metallic iron. When reduction has sufficiently progressed the valves *a* and *b* are closed and the three-way valve *c* is opened. Steam is admitted by the valve *d* and hydrogen is withdrawn at *e*. When the iron becomes reoxidized the steam is shut off and the oxide again reduced by water gas. The reducing gases after passage through the retorts are burned in the combustion chamber. The hydrogen exhibits a purity approaching 98 per cent at a cost of 4 cents per cubic meter.\*

The above concern † employs iron pyrites waste as raw material,

\* *Chemie der Gase*, Brahmer, Frankfort (1911), 93.

† It should be stated that the *Internationale Wasserstoff-Aktiengesellschaft* of Germany is the owner of a considerable number of processes and patents (Iwag System) in the production of hydrogen.

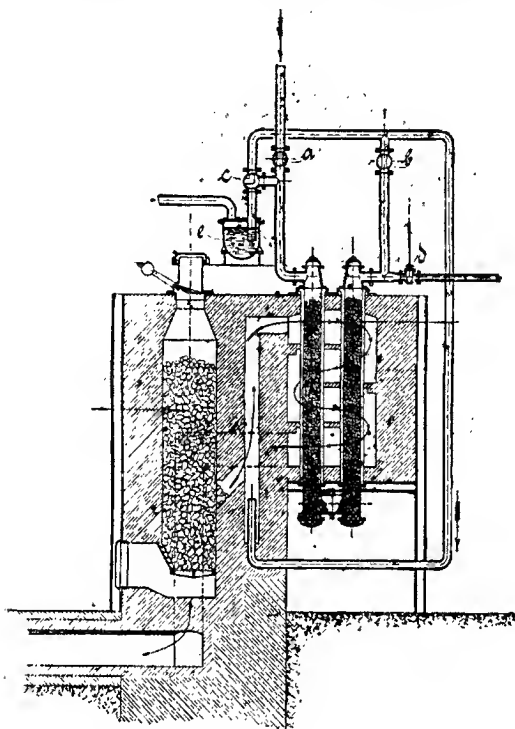


FIG. 79.

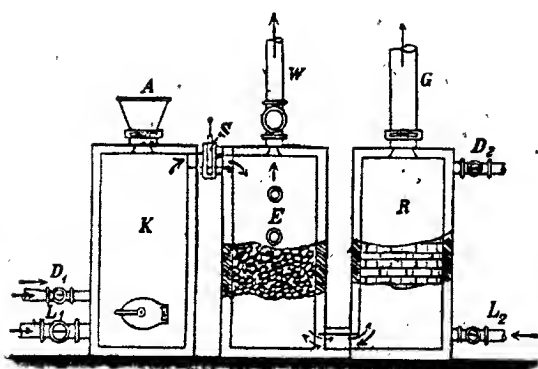


FIG. 80.



which has been deprived of sulfur, arsenic and zinc by roasting; this material is porous and refractory and retains these properties after repeated use.\*

By another process a ferruginous mass is treated alternately with steam and a purified reducing gas, both of which are preheated in regenerators situated outside the reaction furnace, so as practically to avoid transference of heat by conduction from these to the furnace. The reducing gas leaving the reaction furnace is burned with oxygen or air in the regenerators, and the process may be made continuous by employing two or more regenerators with a central furnace, and passing steam and gas through the system, first in one and then in the opposite direction.†

In Fig. 80 is shown a hydrogen-generating apparatus designed by Strache.‡ *K* is a gas producer, the gas from which passes through the reaction chamber *E*, containing iron filings, and is burned in the checkerwork *R*. On passing steam through the checkerwork in a reverse direction the steam becomes superheated and when brought into contact with the iron filings in *E* hydrogen is produced and is withdrawn at *W*. Another apparatus designed by Strache§ is shown in Fig. 81. The water-gas generator 2, provided with inlets 25 and 4, for steam and air respectively is connected with the reaction chamber 6, by the pipe 5, provided with a gas-discharge pipe 24. Just above the place where the pipe 5 enters the reaction chamber is a baffle 22, and on the opposite side of the chamber is a similar baffle 23. A branch from the air-supply pipe opens just below the baffle 22, and similar branches open at 8 and 9. The reaction chamber 6 is divided into compartments by gratings on which the iron reaction material is placed. In the upper part of the chamber, above a regenerator 10, are purifying retorts 11, the gas to be purified entering by 20 and the purified product leaving by 21. When the apparatus has been brought to the proper temperature and is ready for the production of hydrogen, steam is introduced through the pipe 14, below the valve 13, so as to displace any gases from the pipe 5 and the ash-pit 15. Steam is then introduced through the tube 18, below the valve 12, displacing gas from the reaction chamber from the top downwards. The hydrogen produced passes away through 19 to a holder, from which it may be passed through the pipe 20 into the purifying retorts 11, charged with potash lime.

\* French Patent 405,200, July 19, 1909.

† British Patent 2096, Jan. 25, 1913, Badische Anilin und Soda Fabrik.

‡ Brahma, Chemie der Gase, 91.

§ German Patent 253,705, Oct. 26, 1910.



as remedies: the use of fused iron oxides, especially in conjunction with refractory and difficultly reducible oxides of high melting-point such as magnesia or zirconia, the iron oxides being prepared by the fusion of metallic iron in the presence of air or an oxidizing agent; fused iron oxides may be used in conjunction with a silicate as well as similar naturally occurring minerals such as magnetite. The Badische Anilin und Soda Fabrik \* also recommend spongy iron prepared by the reduction of minerals or oxides of iron by means of carbon, employing external heating. The metal is said to retain its porosity after repeated use. "Spongy Swedish iron," prepared in the above manner, is especially suitable.

The Berlin-Anhaltische Maschinenbau-A-G.† has an apparatus for making hydrogen by the iron-sponge system which considerably facilitates the handling of the ore and the regulation of the temperature.

Belou ‡ prepares hydrogen by causing steam (preferably superheated) to pass over red-hot iron in retorts. Hydrogen and oxide of iron are thus formed. The hydrogen passes on to a gas holder for use, and the oxide is reduced to metallic iron again by the introduction of charcoal dust. This latter operation generates so much heat that the retort is again immediately ready for decomposing steam. By using a number of retorts and carrying on the two processes of decomposition and revivification alternately, the production of hydrogen may be made continuous. Suitable provision is made for the removal of the carbon monoxide and dioxide formed during the revivification.

Highly-heated tubes of refractory earthenware, partly filled with iron filings, and in which a partial vacuum has been previously produced, are used by Oetli (British Patent 16,759, Sept. 4, 1885). A certain proportion of hydrogen is added to the steam, and this, together with the action of the iron filings, is claimed to tend to destroy the equilibrium conditions and to prevent the hydrogen formed by the decomposition of the steam from re-uniting with oxygen. This effect is said to be promoted by the reduced pressure in the tubes, and by the loss of heat due to the splitting up of the aqueous vapor. From the tubes the gases pass through separators to gas holders.

Vignon's apparatus § consists of a set of retorts containing iron oxide. A reducing gas is led from a gas producer, through a suitable purifier, into the retorts for the reduction of the iron oxide. The heat formed thereby is utilized for the regenerative heating of the air blast for the producer. The heat of the hydrogen gas produced is used for superheating the steam. A set of four valves can be manipulated

\* French Patent 453,077, Jan. 11, 1913.

† J. S. C. I., 1914, 256, and British Patent, 23,390, Dec. 9, 1913.

‡ British Patent 7518, May 25, 1887.

§ First Addition, dated Dec. 27, 1907, and French Patent 373,271, Jan. 2, 1907.

by a single handle, allowing the regulating and reversing of the different gas currents.

The process of **Gerhartz** \* consists in blowing steam through a molten oxidizable metal, and subsequently reducing the oxidized metal for further use. Molten iron, for example, is introduced into a vessel lined with refractory material and provided with a perforated false bottom somewhat after the manner of the Bessemer converter. Steam under pressure is blown into the space below the false bottom and is decomposed while rising through the molten iron; the hydrogen produced is led off through a suitable pipe, and the heat carried by it is utilized for generating steam. The fluidity of the molten iron is gradually diminished, and after a time the supply of steam is stopped, coke is introduced and the melt is blown with air in order to reduce the iron oxide which has been formed and thus restore the fluidity of the molten mass.

A process brought forward by The Nitrogen Co.† involves reacting with steam on a molten or heated metal having a strong affinity for oxygen, which is thus absorbed. After collecting the residual hydrogen, the metallic oxide produced is made to dissolve or disseminate in a body of fused salt in which it is brought into contact with a suitable reducing agent, the reduced metal being continuously returned for re-oxidation in the process.

Illuminating gas, water gas or other gas containing free hydrogen, according to **Jaubert**,‡ is passed through retorts packed with briquettes formed of iron oxide with a refractory substance and a catalytic agent, the retorts being heated to 800° to 900° C.§ Steam is afterwards passed through the retorts at the same temperature, yielding hydrogen. The briquettes are preferably composed of a mixture of 30 to 60 kilos of iron oxide ( $\text{Fe}_2\text{O}_3$  or  $\text{Fe}_3\text{O}_4$ ), 15 to 25 kilos of fire clay or pumice, 15 to 25 kilos of calcined magnesia and 5 to 15 kilos of the oxide of lead copper, chromium or manganese.

The decomposition of water into hydrogen and oxygen by the action of concentrated solar rays in presence of finely-divided iron and apparatus for effecting this is described by Claver.§

In the manufacture of hydrogen by alternately passing steam over iron, and water gas over the iron oxide thus formed, **Caro** || has devised a system by which portions of the water gas are burned in different

\* German Patent 226,543, June 23, 1909.

† British Patent 17,666, Aug. 3, 1911.

‡ Jaubert, French Patent 418,312, Sept. 23, 1909.

§ British Patent 21,468, Nov. 12, 1895.

|| German Patent 249,269, Aug. 30, 1910.

parts of the reaction chamber, so that in addition to the reduction of the iron oxide, a superheating of the reduced iron is effected. It is claimed that by working in this manner, the gas-making period can be considerably prolonged.

Steam and hydrocarbons (such as those derived from iron carbides) are passed over red-hot iron which has been mixed with (preferably 5 to 10 per cent of) copper, lead, vanadium or aluminium, either together or separately. These metals according to **Saubermann** \* catalytically accelerate the reaction between steam and iron, and also decompose the hydrocarbons.

The action of mixtures of carbon monoxide and hydrogen on iron oxides is discussed by **Gautier** and **Clausmann**.† They passed a mixture of 3 volumes of carbon monoxide and 1 volume of hydrogen at 500° C. over the ferroso-ferrie oxide derived from the calcination of a native ferrous carbonate. The substance formed contained about 7 per cent of carbon, and 93 per cent of ferrous oxide and iron carbides in approximately equal proportions. When steam was passed over this substance at 400° C., a gas was obtained containing 96 per cent of hydrogen and 4 per cent of methane. Over iron (reduced from the oxalate spread over pumice) at 1250° C. was passed a mixture of 2 volumes of carbon dioxide and 1 volume of hydrogen. The issuing gas, besides 23 per cent of carbon monoxide and 76 per cent of hydrogen, contained 0.15 per cent methane.

**Messerschmitt** ‡ recommends as a contact material a mixture of spongy iron and manganese, cobalt or nickel. The mixture may be made by adding the other metal to the spongy iron and is used in powder form or molded into briquettes, or natural ores containing these metals may be used. This mixture has the advantage of not being easily poisoned and may be worked at a lower temperature. Manganese is of special value if a gas containing carbon is used in the reduction stage, for manganese dioxide in the presence of carbon, oxidizes the latter. Superheated steam is passed through the reduced mass and generates hydrogen.§

One form of the apparatus is shown in Fig. 81a.

A shaft furnace for production of hydrogen from iron and steam is described by **Messerschmitt** || in which the annular reaction chamber is divided into sections by vertical projections from the walls or by partitions.

\* British Patent 401, Jan. 6, 1911.

† Compt. rend. (1910), 151, 355.

‡ U. S. Patent No. 1,109,448, Sept. 1, 1914; J. S. C. I., 1914, 962; see also French Patent No. 461,480, 1913; J. S. C. I., 1914, 201.

§ See also U. S. Patent No. 1,152,197, Aug. 31, 1915; British Patent No. 12,117, 1912; J. S. C. I., 1912, 1079; German Patent No. 291,603, Aug. 7, 1913; Chem. Abs., 1917, 983.

|| German Patent No. 291,902, Feb. 12, 1914; J. S. C. I., 1916, 927; Chem. Abs., 1917,

Another method by which Messerschmitt \* generates hydrogen is as follows: The charge of the reaction chamber consists of spongy iron supported on and mixed with compact iron. See Fig. 81b. The supports may consist of plates, grids or screens of iron, upon which is placed iron ore or similar material mixed with short iron bars or other pieces of iron. The charge thus consists of alternate layers of compact iron and spongy iron. In case of melting of the spongy iron the spaces still kept open for the flow of gas and when it becomes necessary to remove the charge, each plate of iron carrying the spongy iron can readily be removed.

In another modification, Messerschmitt † arranges the material in an annular space bounded externally by a refractory furnace wall and internally by a refractory core or checker-work contained in an iron cylinder. By having the reaction mass arranged in a narrow annular column around a central combustion chamber.‡ With a given lateral thickness of material in the column, the ratio between heat-

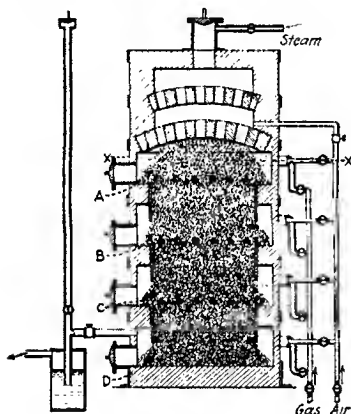


FIG. 81a.

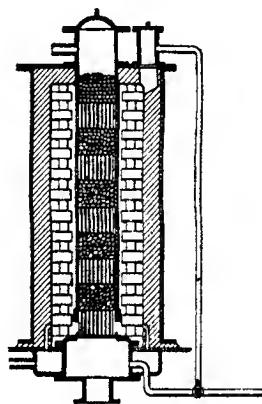


FIG. 81b.

absorbing retort surface and quantity of material is the same whatever the dimensions of the apparatus. Using relatively thin layers of reaction material, a uniform circulation of the various gases through the material is attained more readily than with a retort of large cross-section and on account of the combustion chamber being within the reaction chamber, heat radiation losses are minimized. Fig. 81c indicates the form of apparatus used.

An elaborated form of Messerschmitt apparatus is shown in Fig. 81d. § A pair of concentric cylinders, each open at one end, are arranged in

\* U. S. Patent No. 1,109,447, Sept. 1, 1914, J. S. C. I., 1914, 962.

† British Patent No. 18,942, Aug. 20, 1913; U. S. Patent No. 1,152,196, Aug. 31, 1915; J. S. C. I., 1914, 593.

‡ Messerschmitt, U. S. Patent No. 1,225,263, May 8, 1917; Chem. Abs., 1917, 2142 See also German Patent No. 268,339, of 1912; J. S. C. I., 1914, 137; 1917, 595.

§ U. S. Patent Nos. 1,225,262 and 1,225,264, May 8, 1917; Chem. Abs., 1917, 2141; J. S. C. I., 1917, 595; French Patent No. 444,015, 1912.

the furnace chamber. The ring-shaped space formed between the two cylinders serves to receive the ferrous charge. The furnace space surrounding the outer cylinder and that inclosed by the inner cylinder, are provided with brickwork checkers.

Messerschmitt \* subjects the reaction mass to combined external and internal heating in a modification of the furnace above described. Messerschmitt † also uses a reducing gas comprising a mixture of air and gas produced out of contact with the reaction mass and partly burnt. ‡ Messerschmitt § in still another process produces hydrogen by the alternate reduction and oxidation of iron ores, etc., from iron by means of reducing gases and steam. The heating is effected by a gas of low calorific power, and the reduction by a gas of high calorific power.

Näher and Nöding || describe the following process of generating hydrogen:

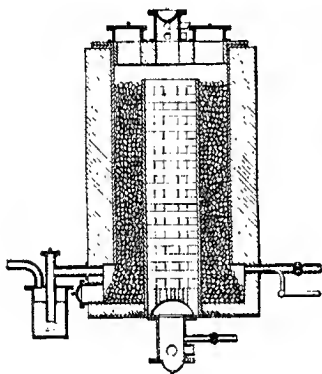


FIG. 81c.

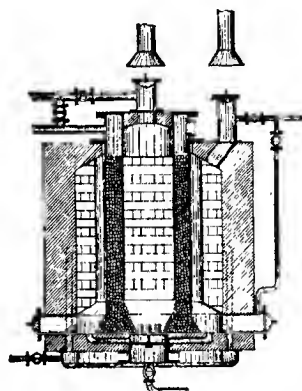


FIG. 81d.

Steam free from air is superheated to about 1000° and passed successively over copper and iron, in a retort heated to about 800° C. To regenerate the metals from the oxides produced, the undecomposed steam from the retort is converted into water-gas, which is passed first over the copper oxide. The gases from the retort are led again into the water-gas generator to reduce carbon dioxide to monoxide and this circulation is continued until the reduction of the metal oxides is complete and carbon dioxide is no longer formed, whereupon steam is again led through the retort to produce hydrogen. Since one volume of carbon dioxide yields two volumes of monoxide, the water-gas generator is provided with a valve by means of which certain proportion of the gas can be withdrawn to be used as fuel. Näher and

\* British Patent No. 17,692, Aug. 1, 1913; Chem. Abs., 1915, 359.

† British patent 17,691, Aug. 1, 1913; J. S. C. I., 1914, 593.

‡ See French Patent No. 461,624, of 1913; J. S. C. I., 1914, 313.

§ British Patent No. 17,690, Aug. 1, 1913; Chem. Abs., 1915, 359.

|| German Patent No. 279,726, Aug. 7, 1913; J. S. C. I., 1915, 355.

Nöding \* in carrying out this process heat the metals to at least 400° C. and the steam to at least 200° C. The metallic oxides produced are again reduced to metal at a temperature of at least 400° C. In the production of the reducing gases, coal, wood charcoal, metallurgical coke, gas coke, or soot, may be used as source of carbon, and small quantities of air, carbon dioxide, producer gas, water gas, or illuminating gas may be added to the steam; the reducing gases are produced at a temperature of at least 400° C.

In connection with their process of producing hydrogen from steam and iron cuttings, Näher and Nöding † prepare cuttings by turning from cast iron with a steel tool held at an obtuse angle to the surface of the cast iron. In this way amorphous iron is obtained, consisting of thin, overlapping, very small flakes, which offer great surface for the action of the steam. Retorts charged with this form of iron may be more quickly heated and less free space is left between the particles of the charge, than is the case with other forms of charge. About six times more iron may be charged into the same space by using this product, and correspondingly more hydro-

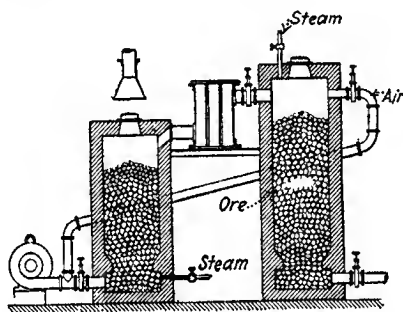


FIG. 81e.

gen is generated. Furthermore, the charge retains its form for at last a week, at 1000°. The furnace is heated by oil and the water gas or generator gas is generated at a high temperature.

Näher and Nöding ‡ construct apparatus for the production of hydrogen from iron and steam by arranging a number of interchangeable cylindrical iron retorts around a tar-oil flame, in a cylindrical furnace. The waste gases are discharged at the bottom of the furnace to avoid losses of the atomized oil. Gas can be generated after an hour's heating.

Spitzer § uses producer gas to heat iron oxide in a generator and then reduces the iron material with water gas. The producer gas is mixed with an excess of air which tends to remove sulphur and carbon from the spongy iron. The same apparatus is used to generate both the

\* German Patent No. 286,900, June 13, 1914. Addition to German Patent No. 279,726; J. S. C. I., 1916, 177.

† German Patent No. 289,207; Chem. Abs., 1916, 2508; J. S. C. I., 1916, 538.

‡ German Patent No. 290,657, Dec. 1, 1914; J. S. C. I., 1916, 602.

§ U. S. Patent No. 1,118,595, Nov. 24, 1914; see British Patent No. 6,155, of 1914; Chem. Abs., 1914, 920, and 1915, 29.



producer gas and water gas. After the iron is reduced superheated steam is passed through the mass and hydrogen produced. The waste gases are used to superheat the steam. In Fig. 81e a gas producer is shown on the right and an ore chamber on the left. Intermediate these two shafts is a purifier which is adapted to hold back dust carried by the gases coming from the producer.

**Schaefer** \* produces hydrogen from steam in an apparatus which consists of a core of coarse material such as iron bars, stones, etc., while the outer portion of the contact substance consists of finer pieces of

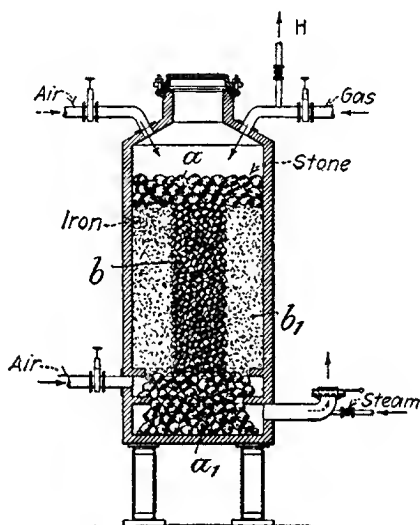


FIG. 81f.

iron. It is claimed that by this method a more equal distribution of heat is obtained than would be were all the particles of the same size.

Fig. 81f is a view of the hydrogen generator, *b* and *b*<sub>1</sub> being the coarse and fine iron material respectively. A layer of stones, *a* and *a*<sub>1</sub>, are placed at the top and bottom to better utilize the heat generated and to give an advantageous control over the reactions which take place.

Schaefer † observes that the combustion of gas of high calorific value must take place with an excess of air, in order to avoid serious

\* U. S. Patent No. 1,144,730, June 29, 1915; British Patent No. 16,140, 1914; Chem. Abs., 1916, 98; German Patent No. 291,022, July 15, 1913; J. S. C. I., 1915, 834; Chem. Abs., 1917, 873.

† U. S. Patent No. 1,172,908, Feb. 22, 1916.

drawbacks. If such a heating gas, for instance water gas, is burnt for the direct heating of iron, with only the quantity of air theoretically sufficient, local superheating is easily produced in the gas generator, which results in a sintering of the pieces of iron with which the flame first comes into contact.

According to Schaefer, for the purpose of avoiding the drawbacks in question, the gas of great heating power is burnt, during the first heating of the iron, with an excess of air as to insure a perfectly uniform heating of the iron charge. As the heating gas, water gas is employed, this requiring for its complete combustion 2.4 times its volume of air. If, however, water gas is burned in the generator and this proportion of air is exactly maintained, Schaefer states that local superheating results, with the adverse consequences above described. If on the other hand an excess of about 25 per cent over the theoretically correct quantity of air is used, i.e., 3 cubic meters of air to 1 cubic meter of water gas, local superheating is stated to be avoided and the charge of iron is heated in a uniform manner.

A hydrogen generator described by Schaefer\* is provided at the bottom with a conical grate below which is a closed heating chamber. A larger number of nozzles or slits can be obtained with a conical than with a flat grate, thus ensuring finer division of the hot gases. The emptying of the shaft is also easier as the conical grate guides the material to the lateral outlets. Schaefer† states that in an installation for the production of hydrogen by the treatment of iron alternately with steam and with a reducing gas previously cooled and purified, the capacity of the apparatus in which the reducing gas is produced and of the cooler and purifier connected therewith, should be so adjusted that the gas may be supplied direct to the hydrogen-producing apparatus, the working pressure being regulated according to the varying back pressure in the section of the plant in which hydrogen is generated and purified. One or more elastic gasholders, placed underground, are interposed between the hydrogen generator and the compressing apparatus to receive excess of hydrogen and supply it to the compressing apparatus when the output of the hydrogen generator is curtailed.

Dempster‡ produces hydrogen by the action of steam on oxidizable material, with alternate reduction by a current of reducing gas (water gas). A pressure-regulating device is provided to prevent leakage of reducing gas into the hydrogen or steam connections, by ensuring a higher pressure in these than in the reducing gas mains. A vessel is divided into two intercommunicating compartments which contain water; one compartment is in connection with the water-gas inlet main and is provided with an overflow passage, while, in the other compartment, water forms a seal between the hydrogen outlet main and the hydrogen scrubber. Any increase of pressure in the water-gas inlet main, acting upon the surface of the water in the first compartment, increases the depth of seal in the second compartment and necessitates therefore a corresponding increase of pressure in the hydrogen outlet main, and in the supply of steam.

**R. and J. Dempster, Ltd.** (Manchester, England), furnish hydrogenating equipment similar to that shown in Fig. 81g. The plant con-

\* German Patent No. 290,529, May 3, 1914; J. S. C. I., 1916, 602.

† J. S. C. I., 1916, 538; German Patent No. 289,208, April 1, 1914.

‡ British Patent No. 16,893, July 16, 1914; J. S. C. I., 1914, 1046; Chem. Abs., 1916, 258.

sists of a blue water-gas equipment, water-gas holder, rotary exhauster, steam engine and purifiers, a hydrogen bench (generators) hydrogen scrubber and purifiers and a hydrogen holder. Steam of 60 to 80 lb. pressure is used. The retorts of the hydrogen bench are heated by means of the blow gases of the water-gas generator. The author is advised that the cost of hydrogen of 98 to 99 per cent purity is about 75 to 90 cents per 1000 cubic feet, with coke at \$3.75 per ton.

The disintegration of iron ore caused by the manner of charging it into the retorts (where it is subjected alternately to the action of reducing gases and steam) is claimed by Dempster\* to be obviated by providing the retort with a perforated platform or

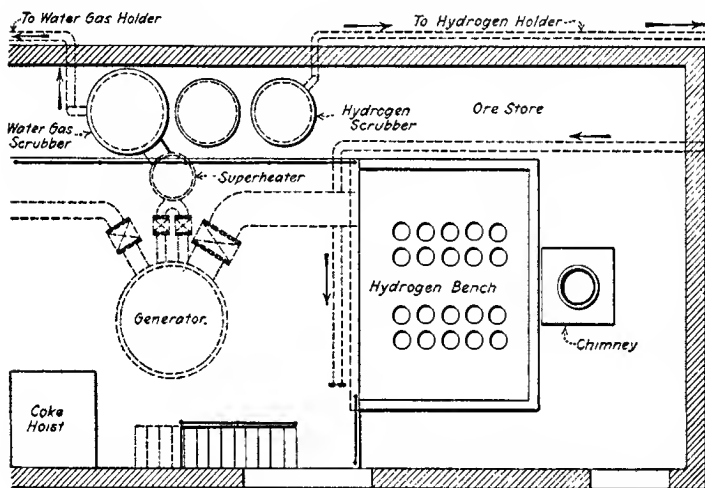


Fig. 81g.

plate, which is mounted on a vertical shaft and can be raised and lowered from top to bottom of the retort for charging and discharging. The movement is guided by projections on the internal walls of the retort, and the platform can be revolved as well as moved vertically.

A method for the treatment and utilization of gases supplied to the furnaces of hydrogen retorts is described by Ballingall (R. and J. Dempster, Ltd.)† according to which, spent water gas from a hydrogen-retort plant is preheated in a regenerator and passed through the reaction zone of a gas producer. The dissociated gas is burnt together with producer gas in the region of the retorts with a deficiency of air so as to form a reducing atmosphere at that point. On leaving this region any unburnt gases are consumed by a further addition of air and give up a portion of

\* British Patent No. 104,115, Aug. 12, 1916.

† British Patent No. 106,067, Jan. 6, 1917; J. S. C. I., 1917, 636.

their heat to the incoming spent water gas in a continuous counter-current regenerator.

**Bosch** \* in the production of hydrogen from steam and iron ore uses three or more furnaces. One of these contains the iron, the other two are preheaters.

The reducing gases are generated and then passed through the iron ore which is partially reduced, the reduction using up part of the gas. The waste gas is mixed with air and passes into the second preheater where it is burned, thus heating the furnace. When reduction is complete, steam is passed through the first furnace where it is superheated and then through the reduced iron mass when hydrogen is generated. In the second cycle the reducing gas is produced in the second furnace, then passed through to the iron ore and the waste gas burned in the first furnace.

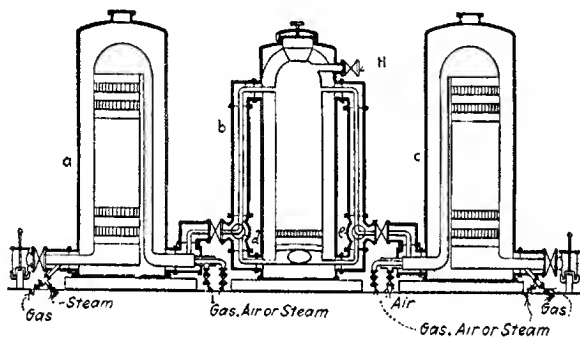


FIG. 81h.

The cycle is then complete and all furnaces are in same state as when the operation was first started. Fig. 81h shows the three-shaft furnaces employed.

**Dicke** † generates hydrogen by the action of steam on scrap from the various departments of an iron and steel works, and the resulting iron oxide is utilized in the blast-furnace or open-hearth furnace. The apparatus is constructed of a refractory chamber surrounded by a tight metal jacket. The chamber is divided into separate compartments by refractory walls. The compartments are arranged with valves, etc., so that they operate independent of each other. They are charged with iron ores or scrap iron and operated in the usual manner. ‡ The apparatus used by Dicke is shown in vertical section in Fig. 81i and in horizontal cross section in Fig. 81j.

According to **Maxted** and **Ridsdale** § hydrogen prepared by passing steam over heated iron previously reduced from its oxide in a current

\* U. S. Patent No. 1,102,716, July 7, 1914.

† German Patent No. 280,964, Aug. 14, 1913; Chem. Abs., 1915, 1531, J. S. C. I., 1915, 492; Chem. Abs., 1915, 1099; U. S. Patent No. 1,129,559, Feb. 23, 1915.

‡ See British Patent No. 29,390, 1913. French Patent No. 465,474, Nov. 28, 1913.

§ British Patent No. 12,698; Sept. 4, 1915; J. S. C. I., 1916, 1060; Chem. Abs., 1917, 538.

of water gas, or other commercial reducing gas, contains considerable quantities of carbon monoxide, due to the deposition of carbon during the reduction and its subsequent oxidation, by the steam.

Hydrogen free from carbon monoxide is obtained by employing for the reduction of the iron oxide a reducing gas containing substantially more carbon dioxide than carbon monoxide, a suitable ratio being 2 : 1. This may be obtained by adding carbon dioxide to water gas, or by suitable modifications in the manufacture of the reducing gas, but dilution of the gas with nitrogen (c.g., by partial combustion of the gas with air) or by steam must be avoided. The presence of carbon dioxide in the reducing gas prevents the deposition of carbon during the reduction of the iron

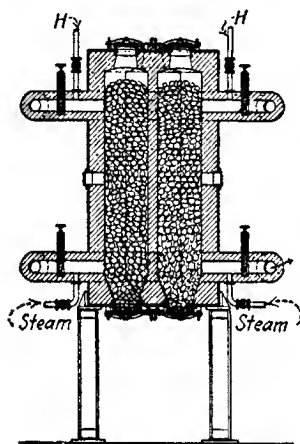


FIG. 81i.

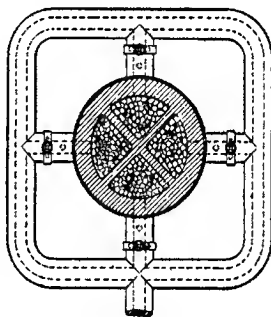


FIG. 81j.

oxide to iron, and, therefore, no carbon monoxide is formed when steam is passed over the heated iron to produce hydrogen.\*

**J. Pintsch Akt. Ges.** † employ pyrite cinder in the manufacture of hydrogen from steam. A ferrous silicate is formed as a result of the reduction of the acid gangue. Such ferrous silicate is quite fusible, acting as a slag and the material is rendered inactive by surface glazing. This disadvantage, as well as the stoppage of the gas passages when basic ores containing limestone are used, is obviated by the employment of compressed artificial stones of iron oxides or carbonates on the one hand, and of oxides or carbonates of magnesium, barium, strontium or calcium-magnesium oxides which possess the requisite porosity.

In a hydrogen generator ‡ operated with iron as the active material, water gas and air are conducted into a shaft filled with iron oxide to preheat and reduce the

\* See also Danish Patent No. 22,122, May 7, 1917; U. S. Patent to Maxted, 1,253,622, Jan. 15, 1918; Chem. Abs., 1917, 2030, and 2721; 1918, 749.

† French Patent No. 466,739, Dec. 30, 1913; Chem. Abs., 1915, 1376.

‡ German Patent No. 283,160, Oct. 31, 1913. J. Pintsch, Akt.-Ges.; Chem. Abs., 1915, 2440.

oxide, and then steam is introduced. The water gas so used is preheated in a pre-heating system wherein the heat from the heating period of the generator is utilized.

According to a process of *Soc. L'Hydrogene* \* the heating gases, before coming in contact with the ferrous material, are passed through a layer of refractory material which serves as a heat accumulator. Any excess of reducing gases leaving the reaction chamber is burnt in a heat recuperator, and the heat utilized to preheat the steam passed in during the subsequent oxidizing stage. Methods to prevent accumulation of oxidizable impurities introduced into the ferruginous mass by the gases employed for heating and reducing are also described.†

Jaubert,‡ proposes a process in which steam is decomposed by metallic iron, and the resulting iron oxide reduced again to the metal by purified water gas (free especially from sulphur compounds) which effects the reduction, at a relatively low temperature, chiefly at the expense of the carbon monoxide present, so that the reaction is almost entirely exothermic. The material to be treated is contained in a series of (preferably three) vertical retorts, which are provided with pipes at either end; the pipes at one end communicate through four-way taps with supplies of steam or purified water gas, and those at the other end of the retorts with the hydrogen receiver or with a residual gas chamber, from which the spent reducing gas (still rich in hydrogen) is distributed to burners projecting within the masonry jackets of the respective retorts. Further external heating is unnecessary.

Hooton§ proposes to treat metallic sulphides and sulphide ores, especially iron pyrites, with steam at 750° to 1000°, the products being porous oxides comparatively free from sulphur, and a mixture of hydrogen, sulphur, water and sulphur dioxide.

The hydrogen is purified, the sulphur being separated during the purification. The pyrites are fed into a retort into which steam is blown. Sulphur condenses in the upper part of the retort and collects in a seal. The gaseous products pass through a hot chamber containing bog iron ore or porous iron oxide obtained by the operation, to induce reaction between hydrogen sulphide and sulphur dioxide, then through a chamber in which sulphur condenses in powder form, then through a cooler preferably containing cold bog iron ore to remove the last traces of hydrogen sulphide and finally through water to remove any sulphur dioxide. The steam may be superheated electrically. To reduce the quantity of water, the gases may be cooled quickly after leaving the retort.

Hydrogen gas or a mixture of hydrogen and carbon monoxide is produced by Tully|| in the following manner: In the lower part of a cylindrical apparatus is a combustion chamber in which a reducing gas is made by blowing air, or air and steam, into incandescent fuel. This chamber extends upwards into a fuel supply chamber, which is surrounded at its lower part by a reaction chamber containing iron ore in direct communication with the combustion chamber by means of holes and passages. Surrounding the upper part of the fuel supply chamber is a steam superheating chamber through which the oxidized gases pass, and which is provided with a valve controlled outlet. After the iron ore has been reduced, the sup-

\* J. S. C. I., 1915, 1054, French Patent No. 474,446, July 1, 1914.

† French patent 472,373, May 19, 1914.

‡ French Patent No. 476,901, May 14, 1914; J. S. C. I., 1916, 635.

§ British Patent No. 18,007, July 30, 1914; Chem. Abs., 1916, 327.

|| British Patent No. 16,932, 1915; J. S. C. I., 1917, 540.

ply of reducing gas is cut off, the outlet pipe is closed, and steam is admitted through a pipe at the top of the apparatus; this passes through the superheater and over the iron, the hydrogen being either tapped through a pipe just below the reaction chamber or passed through the incandescent fuel and led away through a pipe at the bottom of it. Steam or liquid hydrocarbon may be injected directly into the combustion chamber at a point situated between it and the reaction chamber. Air may be admitted at the bottom of the superheater to burn the carbon monoxide, and the heat of combustion utilized to maintain the temperature.

Paraffin hydrocarbons may be dehydrogenated by passage over ferric oxide heated to 580° to 750° C. yielding olefines, terpenes and aromatic hydrocarbons according to **Ramage**.\* The ferric oxide is reduced to ferrous oxide, usually containing some iron. The reduced charge may be regenerated by blasting it with steam at about 150° C. In the course of this regeneration, hydrogen is produced, which Ramage observes may be collected and used for hydrogenation purposes.

### MULTIPLE RETORT SYSTEM †

The apparatus provided for operating this process consists of a combustion chamber containing a number of vertical retorts, the chamber being provided with a gas producer. A combustible gas is delivered from the producer and burned by means of secondary air in the combustion chamber around the outside of the retorts, the products of combustion passing away through recuperators to a stack. The retorts are charged with iron ore of proper grade and sufficiently porous in itself and of proper sized lumps to allow of a more or less free passage of gas. It is necessary that the greatest possible surface of ore be exposed. In conjunction with the retort furnace a blue water-gas generator is provided for the manufacture of the reducing medium. The blue water-gas generator consists of a round shell lined with fire brick in which coke or hard coal is charged, and provided with air blast and steaming connections. The blue water gas is passed to a holder and from the holder to the hydrogen retort furnace. In operation the blue water-gas holder is filled, the hydrogen retorts brought up to heat, and by means of suitable valve connections the steam and blue water gas are alternately passed through the retorts, the resulting hydrogen passing to a holder and the products of combustion passing to the atmosphere. In practice the iron ore in the retorts may be either the ferric oxide,  $\text{Fe}_2\text{O}_3$ , or the ferroso-ferric oxide,  $\text{Fe}_3\text{O}_4$ . In either case the reduction will be back to the ferrous oxide,  $\text{FeO}$ , only a very slight percentage if any of the iron being reduced to the metallic state. The apparatus lasts indefinitely with the exception of the fire-clay lining in the blue-gas generator, which has to be replaced occasionally, and the

\* U. S. Patent No. 1,224,787, May 1, 1917.

† Modified Lane Process of Improved Equipment Co., New York City.

retorts in the hydrogen furnace. These retorts are usually made of cast steel, which seems to be as satisfactory as any material which has been used. Cast-iron retorts have been used with more or less success. The destruction of the hydrogen retorts appears to commence on their outside diameter, working inward more rapidly than from the inside outward. It is obvious that they should fail in this manner as the combustion surrounding the outside of the retorts continually cuts into them, whereas absorption by ferrous oxide of oxygen takes place more rapidly than the absorption of oxygen by metallic iron, and the entire charge of ferrous oxide is changed to the ferric condition before there has been time for the walls of the retorts to be seriously attacked by the oxygen of the steam.

**Bergius** \* describes a process of continuously generating pure hydrogen from iron and water at a low temperature, from 200° to 300° C. The hydrogen is collected in the generator itself in a high state of compression and can be charged direct into cylinders. An example of his process is as follows: 50 kilograms of iron shavings and 265 kilograms iron protoxide and 50 kilograms of water are heated to 300° C. in a closed iron vessel. When the pressure reaches 150 atmospheres the release valve is opened just enough to allow the gas to escape as fast as liberated and to thus maintain the initial pressure. From the above charge 1 cubic meter of hydrogen is given off the first hour. This rate is maintained until about one-half the available gas is evolved, then the rate is somewhat slower. Common salt, iron chloride or small quantities of hydrochloric acid accelerate the reaction, and, in addition, if copper, nickel, or platinum, etc., are placed in the mass, the reaction is accelerated still more and maintains its activity until the iron is converted almost entirely into  $\text{Fe}_2\text{O}_3$ .

One form of generator consists of a pressure vessel within which is a central heating tube and around the latter a series of reaction tubes, each of which can be brought in turn below a feed opening in the cover of the pressure vessel.

**Posen** and **Bergius** † employ a somewhat similar method for the production of hydrogen by the action of water on metals in a closed vessel. The reaction is effected at a temperature below the sintering point of the metal or the solid reaction products, preferably below 500° C. Pure hydrogen is thus obtained in a highly compressed condition, and the yield is nearly quantitative. The addition of electrolytically conducting salts such as sodium chloride is stated to be advantageous.

The decomposition of water by incandescent iron, as also the reduction of the resulting iron oxides by the reducing gases requires a certain temperature of the contact material, which is usually maintained by the continued heating of the furnace containing the iron material, or by passing therethrough hot combustion gases. As a result of the latter practice, the employment of a highly heated gas may occasion

\* U. S. Patent No. 1,059,818, April 22, 1913; German Patent No. 277,501, Nov. 30, 1913, addition to German Patent No. 254,593; French Patent No. 447,080, of 1912; J. S. C. I., 1915, 229.

† German Patent No. 286,961, Nov. 21, 1913; addition to German Patent No. 254,593; J. S. C. I., 1916, 177.



caking of the contact material with consequent loss of contact surface and reduction in the yield of hydrogen. By a process recommended by the **Berlin Anhaltische Maschinenbau Akt. Ges.**\* the required temperature of the contact material is maintained by conducting air through the mass between every double period of reduction and oxidation. In this way heating gas is saved, overheating of the iron charge is avoided, the heating period is materially shortened, and the capacity of the plant is increased. The process is dependent upon the observation that a complete oxidation of the iron material by the steam passed thereover never practically results. Always a portion of iron is left in the metallic state or in a lower state of oxidation. Hence, after the passage of the steam, a current of air is passed through the mass, causing complete oxidation of the iron or of its lower oxides to the higher oxides, with the evolution of considerable heat. The heat so generated is claimed to be sufficient to maintain the normal progress of the reactions. The initial heating of the iron charge is effected by the combustion of gases of high calorific value with excess air, while the periodic reheating is accomplished by the passage of air alone, thereby preventing fusion of the iron. During the oxidation period the steam is introduced highly superheated.†

\* German Patent No. 294,039, May 22, 1913; Chem. Abs., 1918, 410.

† See also French Patent No. 465,575, Nov. 28, 1913; Chem. Abs., 1914, 3491.

## CHAPTER XXIV

### ACTION OF ACIDS ON METALS

One of the oldest methods of generating hydrogen and one which is to-day commonly used in the laboratory and for the production of hydrogen on the small scale is that of acting on metals with acids, iron or zinc and sulfuric acid being the materials usually employed. The cost of generation in this manner is too high to permit of large scale operations except in those cases where hydrogen is obtained as a by-product in the preparation of metallic salts. Accordingly this method of hydrogen generation will be considered only very briefly.

Carulla endeavors to prepare alkali salts, hydrogen and iron oxide, the gas being generated by the action of hydrochloric acid on iron. Instead of using water alone for the absorption of hydrochloric acid in the Le Blanc process, some or all of the receivers or towers are packed with scrap iron or mild steel, ferrous chloride being thus formed and hydrogen evolved. The chloride is then converted, by precipitation, into iron oxide \* and, since very dilute solutions are preferable for this purpose, the absorption of the last traces of hydrochloric acid is rendered very easy by this process, the ferrous liquor plant being conveniently placed at the end of the system, and hydrochloric acid of high strength being produced, if desired, in intermediate parts of the plant.

According to Barton † dilute sulfuric acid is allowed to act on zinc and the zinc sulfate solution produced is filtered and mixed with a solution of sodium carbonate or bicarbonate, thus giving a precipitate which is separated, washed and dried, and sodium sulfate which is also recovered.

The insoluble zinc precipitate is proposed as "an excellent substitute for oxide of zinc used in the paint and rubber industries." The apparatus claimed consists of a generating vessel, communicating with an acid tank by a feed pipe and a return pipe, and also with a gasometer and a mixing tank, the latter receiving the zinc sulfate solution from the generator and sodium carbonate solution from another vessel and communicating, in its turn, with a centrifugal separating and washing apparatus. The generator may be fitted with electrodes for the production of electrical energy.

\* e. g., as in British Patent 27,302, 1908; J. S. C. I., 1909, 1126.

† British Patent 23,534, Dec. 8, 1910.

An apparatus arranged to generate electrical energy when zinc is being dissolved in sulfuric acid to produce hydrogen is set forth by **Eastwick** (British Patent 10,228, April 27, 1911). The apparatus, which is intended specially for the generation of hydrogen by the action of zinc on dilute sulfuric acid, consists of a generating chamber, with false bottom, on which rests the metal to be acted upon, and a liquid-collecting chamber situated below. The acid is delivered by gravitation into contact with the metal at a point near to, but above, the false bottom, and the salt solution produced runs through into the collecting chamber. An electrode may, if desired, be immersed in the liquid, within or below the reaction chamber, so that the apparatus may serve also as an electric cell. An apparatus described by way of example comprises superposed chambers contained within a single casing, the uppermost (containing zinc) and the intermediate chamber being provided with porous or perforated false bottoms. Acid is conducted to the first chamber by a pipe which reaches down through the upper layers of zinc into a cage having lateral perforations, and any excess of pressure forces the acid back in the supply pipe, but the zinc sulfate solution produced percolates into the lowermost chamber. A zinc rod or plate, to act as electrode, is placed above the false bottom in the first chamber and a copper electrode in the intermediate chamber, so that, with the descending liquid, an electric cell, suitable for electro-plating work, etc., is produced, this also ensuring the decomposition of any free acid in the spent liquid.

Hydrogen gas is obtained by **Pratis and Marengo** \* by acting upon iron filings and water by gradual additions of sulfuric acid of 50° Bé., equal parts by weight being taken of each. The hydrogen produced is conducted first through water, then through a solution of a lead salt, and through a device containing diaphragms of wire gauze, to a gasometer, whence the gas traverses an insulating water valve, an elastic chamber and a second device similar to the first, when it is taken by branch pipes to the place of utilization. The arrangements described permit of the gas being produced under considerable pressure.

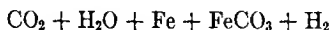
To overcome the difficulties in the way of generating hydrogen from sulfuric acid and iron, **Pratis and Marengo** (British Patent 15,509, June 29, 1907) propose to employ the following approximate proportions, by weight:

Broken iron, 5 parts; water, 5 parts; 50° Bé. sulfuric acid, 5.8 parts; these being found to produce a pasty non-caking residuc, easy to remove from the apparatus and to work up for the manufacture of ferrous sulfate or Nordhausen sulfuric acid.

The apparatus consists of a generating cylinder, fitted with a valve for discharging the residue. The acid and water are run in on to the charge of iron from reservoirs at a higher level, the supply valve being controlled by the bell of the gas holder, and is self-closing when the bell sinks below a certain level; or, if the gas is to be collected in receivers at high pressure, the full charge of liquids may be added at once. Purifiers are arranged between the generator and gas holder, and an excessive rate of generation is prevented by gas checks, which cause an increase of pressure in the generator, whereby the acid is driven back in the supply pipe and the evolution of gas diminished.

British Patent 16,277, July 22, 1896.

The reaction which takes place in the spontaneous formation of iron rust,



may be accelerated by agitation, etc., so as to become a practicable method according to **Bruno** \* for the production of hydrogen. Fragments of cast iron or steel or iron filings were introduced together with water into a steel bottle and carbon dioxide was passed in until the air was displaced and the liquid was saturated with the gas. The bottle was then closed by a steel cover, and placed in an apparatus where it made about 2000 revolutions per hour. There was no appreciable change in the pressure inside the vessel, and after 36 to 40 hours the gas withdrawn from the bottle consisted of pure hydrogen. At the end of 20 hours the gas consisted of about two-thirds of hydrogen and one-third of carbon dioxide.

**Stuart** † describes an apparatus for generating hydrogen by allowing acid to percolate through scrap iron.

The iron is contained in crates which are spaced away from the walls of the generator. The latter may be lined with lead, enamel, etc., to resist the action of the acid. A layer of asbestos which is held between two perforated discs is placed above and below each crate. The acid is introduced under pressure at the top of the generator and percolates through the asbestos and then through the scrap iron. This asbestos serves as a filter for the gas and for the spent acid. Two or more crates of iron scrap may be used in each generator. Fig. 81k shows the construction of the apparatus.

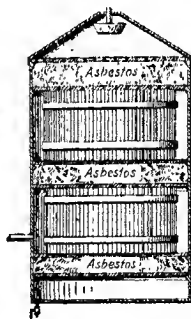


FIG. 81k.

A method of utilizing the acid values of sodium acid sulphate or bisulphate is recommended by **Becquevort** and **Deguide** ‡ as follows: A solution of sodium bisulphate of density 20° Bé. (sp.gr. 1.16) is added to scrap iron in a suitable tank and heated by steam to 90° C. The liberated hydrogen is washed and collected in a holder. The resulting solution of ferrous and sodium sulphates is treated with an excess of powdered lime, producing a mixture of calcium sulphate and ferrous hydroxide, which is aerated to convert the latter into ferric hydroxide. The mass is filter-pressed, and the solution flowing away is concentrated to 30° Bé. (sp.gr. 1.26) and Glauber's salt separated by crystallization. The material left in the filter-press is used as a gas-purifying agent.

**Curran** § in discussing the electrolytic generation of hydrogen, states that savings

\* Bull. Soc. Chim. (1907), 1, 661.

† U. S. Patent No. 1,085,366, Jan. 27, 1914.

‡ British Patent No. 107,807, July 11, 1910; J. S. C. I., 1917, 962; Chem. Abs., 1917, 2947.

§ Eng. Mining J., 1917, 158.

and improvements in service of the electrolytic method over the zinc-sulphuric acid method are most marked. The operating cost of an electrolytic plant is one-fifth that of a zinc-acid plant and there are no acid-eaten hydrogen pipes or freeze-ups in winter. The most economical rate of generation under the conditions employed by Curran was at 400 amperes and 36 volts with the temperature at 53°. Caustic soda solution of 26° Bé. was used as an electrolyte. Equipment and layout of plants are given.

## CHAPTER XXV

### MISCELLANEOUS METHODS OF HYDROGEN GENERATION

Much attention has been given to the production of hydrogen by chemicals, which, when added to water or hydrated substances, would liberate hydrogen freely, thus enabling the generation of hydrogen at any point without the necessity of setting up elaborate apparatus. Powdered aluminium or silicon and alkali, "activated" aluminium and water, ferrosilicon and calcium hydrate, calcium hydride and the like have been proposed under various names such as hydron, hydrogenite, the Hydrik process, etc. Bergius has brought out a novel process involving the treatment of carbon or iron with water in a liquid condition under very high pressures. The following indicate the principal developments in this direction.

Foersterling and Philipp\* generate hydrogen by causing water, in a finely-divided state, to react successively with relatively small masses of sodium, separated from each other, in the same containing vessel, in such a way that the supply of hydrogen is continuous, and at a rate that substantially prevents a solution being formed. They also propose silicides for the generation of hydrogen.† An intimate mixture of equal parts by weight of sodium and aluminium silicide ("sical") is prepared by heating the two substances in a kneading machine until all the sodium is molten; the kneading appliance is then put into operation and kept continuously rotating while the mixture cools down, after which the latter is transferred to a press and briquetted. One kilo of the mixture, when acted on by water, generates about 700 liters of hydrogen, the reaction being represented by the equation,



Brindley and Bennie (U. S. Patent 943,036, Sept. 14, 1909) use a mixture consisting of finely-divided aluminium and molten sodium hydroxide, the proportion of the latter being between 1 and 3 mols. to 1 mol. of aluminium. Silicon and zinc may also be added.

Brindley (U. S. Patent 909,536, Jan. 12, 1909) treats an alkali or alkaline-earth metal, for example sodium, in a finely-divided state, with a crude hydrocarbon oil

\* U. S. Patent 883,531, March 31, 1908.

† U. S. Patent 977,442, Dec. 6, 1910.

or similar substance, which will temporarily prevent oxidation of the metal, and with an inert substance such as infusorial earth, and the mixture is compressed into tablets or briquettes, which when brought into contact with water will generate hydrogen. In order to increase the yield of hydrogen, a metal (aluminium, silicon) which forms a hydroxide, the hydrogen of which can be replaced by an alkali or alkaline-earth metal, is also incorporated in the mixture.

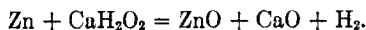
**Philipp** (U. S. Patent 1,041,865, Oct. 22, 1912) generates hydrogen by the action of water on a mixture of metallic sodium and aluminium silicide. The action of water on this mixture does not proceed to completion, and the method consists in first treating the mixture with water, and then passing the hot hydrogen and steam through a similar mixture which has previously been partially decomposed by treatment with water.

**Jaubert** \* suggests that the hydrogen evolved in such industrial processes as the production of electrolytic soda, be collected, deprived of any oxygen present (as by passage over red-hot copper), dried, directed into an iron tube charged with calcium in small pieces, and heated for some hours to redness. The dark grey calcium hydride thus obtained is preserved in closed vessels. When the hydride is brought into contact with cold water, there is a violent evolution of hydrogen.

**Bamberger, Bock and Wanz** † generate hydrogen from calcium hydride which is mixed with substances such as gypsum, sodium bicarbonate, soda-lime or boric acid, which contain water or carbonic acid, but which react only when heated to about 80° C., or a higher temperature.

Gases which are prepared by the action of a liquid upon a solid, for instance, hydrogen by the action of water on calcium hydride, are obtained pure and free from the water vapor which is frequently generated by the heat of the reaction, in the following manner: The solid is placed in a connected series of separate vessels, or in superposed compartments of the same vessel, and the liquid is admitted to the first, or lowest, of the series. The gas given off, along with some vapor of the liquid, passes through the next vessel, or compartment, and so through the series and leaves the last in a dry condition, the water vapor having been retained by the fresh material. When the first vessel is exhausted it is recharged and connected to the end of the series, the second vessel becoming the first. In this way the process becomes continuous.‡

**Schwarz** § describes two simple methods for preparing pure hydrogen gas and carbonic oxide. On heating a mixture of zinc dust and calcium hydrate gradually in a combustion tube, a constant current of pure hydrogen is liberated according to the equation,



\* French Patent 327,878, Dec. 31, 1902.

† German Patent 218,257, March 31, 1908.

‡ Jaubert, French Patent 381,605, Nov. 14, 1907.

§ Ber., 19, 1140.

On mixing the zinc dust with calcium carbonate in molecular proportions and heating as before, pure carbonic oxide gas is evolved thus:

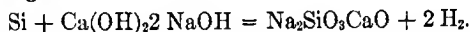


In both cases nearly theoretical quantities of gas are obtained.

Hydrogen is produced by the process of **Jaubert** \* by ignition and autocombustion in a closed generator, of a mixture consisting of an excess of a combustible substance (metal, metalloid or alloy), capable of decomposing steam at a high temperature, an oxidizer or other substance to maintain the combustion, and a substance evolving steam on heating (which is omitted, partially or wholly, if steam be introduced from an external source).

Suitable mixtures, which may be packed in metal cartridges, to be opened and placed directly in the generator, are the following: (a) Powdered iron 20 kilos, slaked lime 10, potassium perchlorate 6, (b) ferrosilicon, with 75 per cent of silicon, 20, litharge 10, soda-lime, containing two-thirds of sodium hydroxide 60; (c) ferrosilicon 20, powdered iron 5, wheat flour 3, lime 5, and potassium chlorate 3. If the ingredient evolving steam be omitted, the generator may be surrounded by a water jacket, the two vessels being connected so that the necessary steam is supplied from the latter by the heat of the reaction; a pipe from the generator conveys the gas either to the exterior or through a purifying and drying apparatus, to be utilized. The generator described is closed by a heavy lid which, for safety, is held in position by its own weight.

The **Hydrogenit** process of Jaubert † involves mixing finely-powdered ferrosilicon with soda-lime to produce a grayish granular mass which easily ignites and burns readily even with the exclusion of air, the reaction being



From 3 kilos of the mixture, which, by the way, is stable at ordinary temperature, about 1 cubic meter of very pure hydrogen is obtained. The mixture is pressed to blocks and is shipped in metal containers holding 25 to 50 kilos, affording 8 to 16 cubic meters hydrogen in about a ten-minute period. The mixture is kindled by a small amount of ignition powder or quick-match. Equipments for furnishing 150 cubic meters hydrogen per hour have been made. The generators are arranged in pairs, see Fig. 82.

A case of hydrogenit is placed in each generator. The cover of the generator is put on and clamped in place and the mixture lighted through a closable opening in the cover. The generators are equipped with water jackets and the steam produced by the heat of the reaction is, towards the end of the run, turned into the

\* French Patent 427,191, May 21, 1910.

† German Patent 236,974.



generator, giving a larger yield of hydrogen. The gas is washed and dried. One cubic meter of hydrogen made from Hydrogenit costs about 32 to 38 cents.\*

Jaubert (French Patent 422,296, Jan. 14, 1910) has described the following modification of the above. Metals such as aluminium or zinc, or their alloys, or metalloids such as silicon or carbon, or their compounds, e.g., ferrosilicon, when mixed with alkali or alkaline-earth hydroxides in the form of dry powders, yield mixtures quite stable at ordinary temperatures. If, however, reaction be induced by local application of heat, hydrogen is evolved and sufficient heat is developed to cause the propagation of the reaction throughout the mass. A suitable appara-

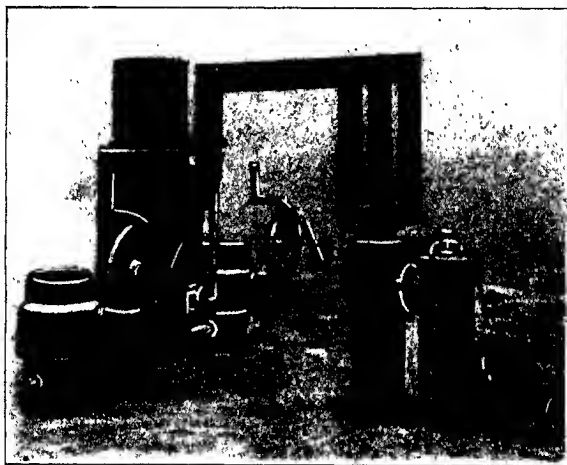


FIG. 82.

tus consists of a tube closed at one end by a screw cap and having near this end an opening (with a screw cap) through which a quick-match or piece of hot iron may be introduced to induce the commencement of the reaction. The other end of the tube is formed by a perforated plate, through which the hydrogen evolved passes into a chamber packed with filtering material, and thence into an annular space formed between the tube and a jacket extending nearly the whole length of the latter. The hydrogen accumulates in this annular space under pressure, and is withdrawn as required through a suitable outlet.

Ferrosilicon containing 75 per cent of silicon, when heated to a very high temperature is capable of decomposing steam with sufficient evolution of heat to carry on the reaction,



(Jaubert, French Patent 438,021, March 4, 1911.) The reaction may be regulated by the addition of lime, which has the further advantage of forming an easily-workable slag. The apparatus comprises a refractory chamber surrounded by a steam coil, the delivery end of which terminates in a series of injectors, which admit steam

\* *Zeitsch. f. angew. Chem.* (1912), 2405.

into the chamber; a feeding hopper is provided at the top of the chamber and a door for the withdrawal of the slag at the bottom.

An alkali or alkaline-earth hydroxide, or a mixture of the two, is mixed with charcoal and a finely-divided metal or mixture of metals, and the whole is heated in a hermetically-sealed vessel, with the exclusion of air, and under diminished pressure. Under the action of the metal, according to Hlavati (German Patent 250,128, Feb. 25, 1911) the hydroxide is converted into oxide, and hydrogen and carbon monoxide are formed.

The **Siemens & Schuckert Company** has worked out a process for the production of hydrogen from the reaction between silicon and caustic soda solution. Formerly steam was employed, but now the heat set free during the reaction is utilized for maintaining the proper conditions. The evolution of hydrogen gas takes place when a 25 per cent solution of caustic soda acts on silicon introduced in small quantities. The capacity of a transportable plant is 60 to 120 cubic meters per hour, while stationary plants are built for capacities up to 300 cubic meters per hour. The process is a neat one, but the cost is about 18.75 cents per cubic meter.\*

A somewhat similar system is used in France under the name of the **Silicol** process. Ferrosilicon or other silicon alloy is treated with freshly-prepared 35 to 40 per cent caustic soda solution. The heat of solution of the alkali raises the temperature to 60 to 80 degrees and enables the reaction to progress rapidly. Hydrogen by this method costs about 20 cents per cubic meter.†

By the **Hydrik** process aluminum powder is acted on by caustic soda giving hydrogen and sodium aluminate, according to the equation,

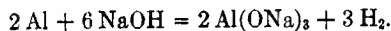


Fig. 83 shows a gas generator for the Hydrik process with an hourly capacity of 10 cubic meters.

By the addition of lime, or calcium compounds that form lime, according to ‡ **Consortium für Elektro-chem. Ind. ges. m. b. H.**, nearly the full theoretical quantity of hydrogen is rapidly liberated on heating silicon in an aqueous solution of caustic alkali. The process may be carried out in an iron generator fitted with stirrers, and in British Patent 11,640, May 13, 1911, it is stated that the temperature necessary for the generation of hydrogen from silicon and caustic alkali solutions may be obtained by the solution of the powdered alkali or alkali oxides in water, or by the heat produced in the chemical reaction between aluminium or aluminium alloys and the alkali.

\* Met. and Chem. Eng. (1911), 157.

† See *Zeitsch. f. angew. Chem.* (1912), 2405.

‡ British Patent 21,032, Sept. 14, 1909.

Jaubert (French Patent 430,302, Aug. 6, 1910) uses a strong solution of a caustic alkali, or a solution of sodium or potassium sulfate containing such, which is made to act upon a compound or alloy of silicon (preferably ferrosilicon, manganosilicon or silicospiegel) in such a way, that the heat produced in preparing the alkali solution is utilized in effecting the reaction, no external heat being required. The reaction takes place in a generating vessel, fitted with a stirring device and surmounted by a feeding hopper containing the powdered alloy; this vessel communicates both with an arrangement for washing and cooling the gas and with another vessel, also provided with a stirrer, in which the solution of caustic alkali is prepared (e.g., by dissolving 1 part by weight of sodium hydroxide in  $1\frac{1}{2}$  to 2 parts of water). The

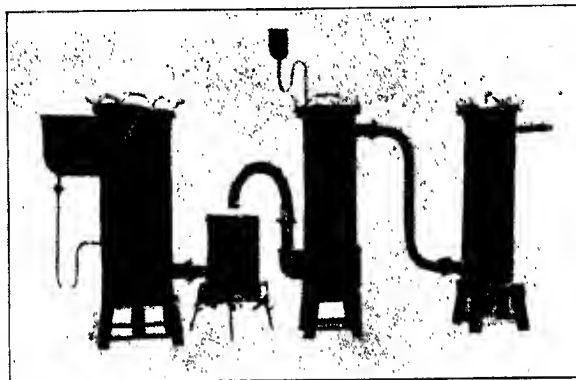


FIG. 83.

water which has served to cool the gas in the condenser passes either to the generator or to the dissolving vessel. A strong solution of alkali being used, an acid silicate is obtained, moreover, non-caustic residues, suitable for use in dyeing and bleaching, are obtained.

The preparation of hydrogen under pressure by the wet method is detailed by Jaubert\* as follows:

The reaction by which the hydrogen is produced is carried out under a pressure above the vapor pressure of water at the temperature in question, the larger part of the heat produced is localized and stored in the reacting liquid, and by preventing the vaporization of this liquid, dry hydrogen is obtained, the speed of manufacture is increased, and the amount of liquid necessary for the reaction diminished. The pressure is produced automatically by working with an autoclave generator, in which the hydrogen produced is allowed to accumulate. The generator is a revolving cylinder, provided with an autoclave cover, a charging chamber which penetrates some distance into the interior of the cylinder and a blow-off cock, so that complete mixing of the reagents can be prevented before the reaction is started and to allow the hydrogen formed to be drawn off.

To obtain a rapid and constant evolution of hydrogen by the interaction of silicon, aluminium or alloys containing the same, with an alkali hydroxide, Jaubert (French Patent 454,616, April 30, 1912) prepares an emulsion of a concentrated

\* French Patent 433,400, Oct. 25, 1910.

solution of the latter with a non-saponifiable oil or grease, such as paraffin, which mixture is heated to 100° C., with the elements or alloys named, in the form of fine powder, water being added as fast as it is decomposed, and the frothy mass being kept constantly agitated.\*

**Mauricheau-Beaupre** † adds to fine aluminium filings a small proportion of mercuric chloride and potassium cyanide, which causes a slight rise of temperature and produces a coarse powder, quite stable if kept from moisture. This powder is treated with water (about 1 liter to a kilo) and the rise of temperature which occurs as the hydrogen is evolved is watched, and regulated if necessary by the addition of more water so that the temperature does not rise above 70° C. At this temperature 1 kilo of the powder is completely oxidized in about two hours.

The advantages of this method are that the apparatus needed is of the simplest description, and can be made of almost any materials, as the products are perfectly neutral; that the gas produced is pure; and that a very large volume is yielded by a small weight of volume of the reagent (1 kilo yields 1300 liters, or 1 cubic decimeter 1770 liters). Pure aluminium filings with 1 to 2 per cent of mercuric chloride and 0.5 to 1 per cent of potassium cyanide should be used. (French Patent 392,725, July 27, 1908.) Aluminium hydroxide is obtained as a by-product.

**Chem. Fabr. Griesheim-Elektron** ‡ recommend a preparation consisting of finely-divided aluminium (98 parts) mixed with small quantities of mercuric oxide (1 part) and caustic soda (1 part). On treatment with water, hydrogen is evolved steadily and uniformly, 1 to 1.2 cubic meters (calculated at 0° C. and 760 mm.) being obtained from 1 kilo of the product. The mass can be kept unaltered for a long time if protected from moisture, and can be easily transported, 1 kilo occupying a volume of only 0.8 liter. The cost is about forty-five cents per cubic meter.

In the corresponding British Patent 3188, Feb. 9, 1909, it is stated that aluminium in a divided form, such as filings, dust, chips or factory waste, is mixed with a small quantity of a compound of a metal such as mercury, which is electro-negative to aluminium, and with a small quantity of an alkali or acid, or a borate, phosphate or other soluble substance. The alkali, etc., serves to generate sufficient hydrogen to reduce the mercury or other compound, which then forms an electro-chemical couple with aluminium and decomposes water until the aluminium is used up.

According to **Uyeno**, § 78 to 98 parts by weight of aluminium are melted in a crucible and a mixture of 15 to 1.5 parts of zinc and 7.0 to

\* See also U. S. Patents to Jaubert: 943,022, Dec. 14, 1909; 1,029,064, June 11, 1912; 1,037,919, Sept. 10, 1912; and 1,040,204, Oct. 1, 1912.

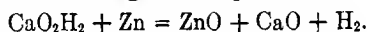
† Compt. rend. (1908), 147, 310.

‡ German Patent 229,162, Jan. 17, 1909.

§ British Patent 11,838, May 18, 1912.

0.5 part of tin are added to the molten metal, after which the alloy is cast in the form of a plate. For each part of this alloy 0.12 to 0.025 part of mercury, or a quantity of zinc or tin amalgam containing this amount of mercury, is taken and amalgamated with the upper and lower surfaces of the plate by rubbing it in with a steel brush. The plate is then heated to as high a temperature as possible without volatilizing the mercury, until the alloy has become uniformly amalgamated, whereupon it is ready for the manufacture of hydrogen by acting on it with hot water.

When zinc dust is heated with hydrated lime, as previously stated, hydrogen is formed according to the equation,



On this reaction **Majert** and **Richter** \* have based a technical process of generating hydrogen, in which they employ apparatus as shown in Fig. 84. A heating chamber *F* carries a series of horizontal tubes

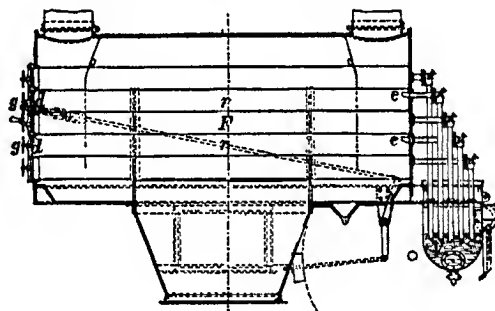
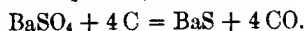


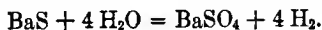
FIG. 84.

*r*, each of which is provided at one end with a gas eduction pipe *e*, leading to a water seal *V*, and at the other end with a removable cap. Iron or carbon may be used in place of zinc.

In the **Lahousse** process † coal, mixed with barium sulfate, is heated at a red heat so as to produce carbon monoxide and barium sulfide, according to the equation,



The sulfide of barium produced is then heated to redness in a current of steam, with re-formation of barium sulfate and evolution of hydrogen.

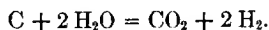


\* **Brahmer**, *Chemie de Gase*, 101.

† French Patent 361,866, Oct. 24, 1905.

The regenerated barium sulfate is ready for use *de novo*. The carbon monoxide produced in the first operation may be employed for heating the retorts. Lahousse also states that sulfate and sulfide of strontium may be used in place of the corresponding barium compounds.\*

The **Bergius** process. Steam acts on incandescent carbon to produce hydrogen and carbon monoxide. Below 650° C. carbon dioxide instead of carbon monoxide is formed to some extent according to the reaction,



Bergius has found that this reaction occurs almost exclusively if water at a temperature of about 300° C. is allowed to act on carbon under a pressure sufficient to keep the water in a liquid state. The addition of small amounts of thallium salts is beneficial as the reaction is thereby promoted through catalytic action. In order

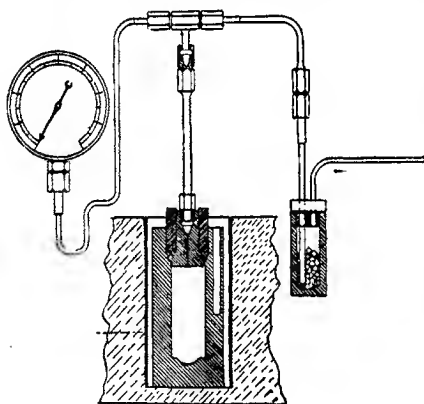


FIG. 85.

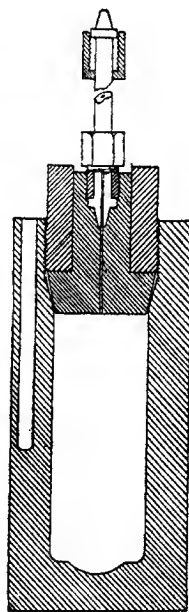


FIG. 86.

to work under the high pressures necessitated by these considerations Bergius has made use of apparatus as shown in Figs. 85 and 86.

The successful closure of the reaction chamber was attained by the use of a tapered plug forced into a seat having a taper of different angle so that the contact becomes a line rather than a surface. (Bergius, *Die Anwendung hoher Drucke bei Chemischen Vorgängen*, Halle, 1913, 6.) A charge of say 100 kilos coke and 200

\* First Addition, Oct. 23, 1905, to French Patent 361,866.

kilos water containing in solution 1 kilo of thallium chloride is placed in a strong iron vessel provided with a valve, and the vessel is heated to  $340^{\circ}\text{C}$ . (German Patent 259,030, June 24, 1911.) The mixture of hydrogen and carbon dioxide which collects in the upper part of the vessel is blown off through the valve at intervals of half an hour, and the carbon dioxide is absorbed by lime.

Using iron instead of carbon, Bergius\* has developed a process of making hydrogen without the accompanying formation of carbon dioxide, based on the reaction between iron or other metal and water at a temperature of  $300^{\circ}\text{C}$ ., or so.† A receptacle as shown in Fig. 87 is employed. This has an expanded basal part serving as a reaction chamber and a long tubular outlet.‡

Iron and water (which should contain an electrolyte such as sodium chloride) are placed in the chamber and are heated to  $300^{\circ}\text{C}$ . The pressure rises to 100 atmospheres or higher. Water condenses in the tubular outlet and flows back into the reaction zone. Hydrogen is blown off by means of the valve in the upper part. It is stated that in this way hydrogen can be obtained directly

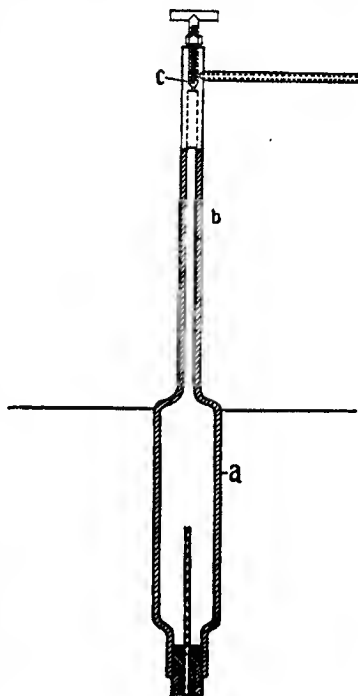


FIG. 87.

\* Bergius (*Zeitsch. f. angew. Chem.* (1913), 517) states that with his process hydrogen containing less than 1/100 of a per cent of impurities may be produced. In apparatus which has been thoroughly tested at Hanover, a vessel of a capacity of 80 liters produced 12 cubic meters of hydrogen hourly. Bergius states that the construction of vessels of larger size up to a capacity of about one cubic meter offers no difficulty. In large plants which are arranged for proper heat utilization, Bergius estimates the cost of hydrogen at about 2 cents per cubic meter. The advantage of this process is that very pure hydrogen under high pressure may be produced at a low cost and without an expensive equipment, enabling works requiring only a small amount of hydrogen to produce this gas on the spot at low cost. The iron oxide formed by the reaction can be reduced by heating with carbon at  $1000^{\circ}\text{C}$ . and is then ready to be used a second time.

† German Patent 254,593, Oct. 24, 1911, and German Patent 262,831, July 7, 1912.

‡ Apparatus fitted with an agitator and adapted for the treatment of liquids with gas under high pressures is described in *Chem. Ztg.* (1913), 1288.

under a pressure more than 100 atmospheres. Lower oxides of metals may replace the metals themselves. (French Patent 447,080, Aug. 9, 1912.) The water may contain neutral salts, acids or other conductive compounds. The reaction is also accelerated by the use of a second metal, such as copper, nickel or platinum, more electropositive than the principal metal.\*

**Sabatier** † produces a mixture of hydrogen and methane by passing moist purified water gas over finely-divided nickel at a temperature of from 300 to 450° C. The water gas is first purified by removing carbon dioxide by means of sodium carbonate and caustic soda or potash, and is then passed over copper to remove sulphur.

Sabatier observes that the manufacture of methane or of mixtures of methane and hydrogen has been carried out by producing water gas, by depriving the gas of carbon dioxide with the aid of an alkaline carbonate and by finally passing the gas over heated nickel. This process has never produced good practical results on account of the following reasons: The water gas constantly varies in composition and as the whole operation is based on a definite composition of the gas, the process soon becomes defective, the production of hydrogen becomes insufficient, the nickel is carbonized and after a short time the operation has to be stopped. The carbonized nickel has to be regenerated and an operation of the kind requires time and expense.

**The Reaction in the Nickel Tubes.** The practical execution of this reaction depends on the following conditions: 1. The initial cleaning of the gas. 2. The arrangement of the apparatus. 3. The preparation of the nickel. 4. The way of conducting the operation.

1. The gas deprived of carbon dioxide consists of a mixture of carbon monoxide and hydrogen. It must be freed from traces of sulphur compounds that it may contain and for this purpose the gas is made to pass through tubes, Fig. 87a, containing copper in the shape of turnings or of a fine powder. These tubes are built into a water-gas furnace and must be maintained at a temperature between 500° and 600° C. The copper heated to dark red withholds any impurities that might deteriorate the nickel. After long use the copper becomes partly transformed into copper sulphide and must be renewed. 2. The apparatus for the reaction with

\* *Badische Anilin und Soda Fabrik.*, French Patent 441,695, March 23, 1912. Operations in which hydrogen, or gases containing it, are employed under pressure and at a high temperature can be carried out in vessels, provided with special strengthening appliances, although the wall of the interior vessel in which the reaction takes place is composed of some material, such as iron free from carbon or nickel, which is incapable of offering by itself sufficient mechanical resistance to the conditions imposed by the process, but chemically is as resistant as possible to hydrogen. (See also U. S. Patent 1,077,034, Oct. 28, 1913; and 1,075,085, Oct. 7, 1913.)

Hydrogen under pressure may be used in conjunction with vessels constructed of steel alloys at temperatures considerably above 450° C. when these alloys contain certain proportions of chromium, vanadium, tungsten, molybdenum or the like. Suitable alloys contain (1) tungsten 18 and chromium 3 per cent, and (2) chromium 2.9 and carbon 0.2 per cent. Alloys containing too high a percentage of nickel should be avoided. (J. S. C. I. (1913), 1010; *Badische Anilin und Soda Fabrik.*, British Patent 29,260 and 13,258, Dec. 19, 1912, and June 7, 1913.)

† U. S. Patent No. 956,734, May 3, 1910.



nickel consists of horizontal metallic flattened tubes. 3. The nickel producing the catalytic reaction must be in a powdered condition and is obtained by reducing commercial nickel oxide. The oxide is reduced by applying the mixture of carbon monoxide and hydrogen that issues from the copper tubes. The reduction is effected between 350 and 450° C. 4. The tubes for the nickel are grouped in several series

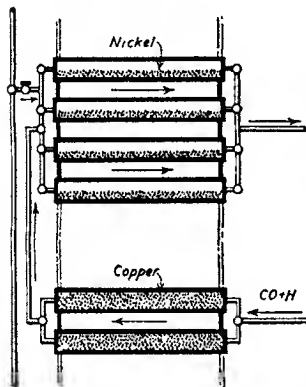


FIG. 87a.

that are independent of one another, so that one series may be emptied, filled again and reduced without interrupting the whole operation. 5. The reaction with nickel is effected at 350° C., but the temperature may vary between 300° and 450° C. without involving any serious disadvantage. As the gases are moist when they reach the nickel and the reaction is accompanied by a considerable production of water, the permanent formation of carbon on the nickel according to the reaction  $2\text{CO} = \text{C} + \text{CO}_2$  does not take place.

Jaubert \* tests silicol (ferro silicon) and other silicon alloys used in the production of hydrogen, by the following procedure: Five portions (10 g. each) of the ferrosilicon contained in thin paper thimbles are added successively to 50 cc. of 40 per cent sodium hydroxide solution in a 2-liter flask and kept

at 80° C. The evolved gas is led through three wash bottles containing, respectively, pure water, bromine water (to oxidize hydrogen phosphide) and 10 per cent sodium hydroxide solution (to remove bromine vapor). To the last wash-bottle, in which a thermometer hangs, is connected a gas receiver. The volume of gas obtained is reduced to 0° C. and 760 mm. 50 g. of silicol yield 70 to 75 liters of hydrogen.

Baillio † produces hydrogen and sodium silicate by the following method. An excess of silicon is repeatedly acted on with 10 per cent caustic soda solution, in a closed vessel and the hydrogen and sodium silicate solution produced by each treatment are removed before adding fresh caustic soda solution.

De la Fresnaye and Suchy ‡ give the following as a cyclic process for producing nascent hydrogen by means of esters.

An ester is saponified with water, in the presence of a metallic oxide or carbonate and the material to be treated with nascent hydrogen, to which may be added a reducing agent, such as trihydroxybenzene or gallic acid. For example, petroleum containing sulphur compounds is treated with ethyl acetate, lead oxide or carbonate, and a small proportion of trihydroxybenzene, the lead sulphide produced

\* Rev. Gen. Chim. pure et appl., 1913, 16, 341; Chem. Techn. Rep., 1914, 38, 380; J. S. C. I., 1914, 1091.

† Chem. Abs., 1916, 1582, J. S. C. I., 1916, 633. U. S. Patent No. 1,178,205.

‡ French Patent No. 476,454, Apr. 23, 1914; J. S. C. I., 1916, 48.

is filtered off, and ethyl acetate, which is continuously reformed, during the reaction is recovered by fractionating the filtered product; the reaction is facilitated by adding ether to prevent emulsification.

**Kessener \*** produces hydrogen by the following method: Waste liquor sludges, or the liquors themselves (e.g., from paper factories), are inoculated with anaërobic bacteria capable of producing methane or hydrogen, selected with special regard to the nature of the particular waste liquors employed. Suitable nutrient salts are added and the bacteria are grown under conditions which minimize the production of free nitrogen.

In **Snelling's** process † hydrogen is separated from producer gas or other gases by diffusion through porous earthenware or alundum containers having a thin coating of platinum or palladium. The porous tube is electrically heated by resistance wires preferably to above 800°, the gas being introduced under pressure. Hydrogen diffuses through the platinum or palladium film and porous tube and is then drawn off. Several other forms of apparatus are also described. Cobalt, nickel or iron may be used instead of platinum or palladium but with decreased efficiency.

The separation of the different components of a gas mixture is brought about by **Wussow ‡** by leading the gas over the surface of permeable or absorbing media. These media may be either solid or liquid, and different forms may be used simultaneously to separate the different constituents of a complex mixture. Moving permeable surfaces may be used to accelerate the diffusion. The diffused gas may be removed from the farther side of the diaphragm by maintaining a low pressure or by circulating an indifferent gas, such as steam, ammonia, or carbon dioxide, which afterwards can be removed by solution or condensation. Diffusion may also take place through several media in succession, each of which causes a partial separation. As an example of the process, using a layer of water as permeable medium, at 0° C., this would absorb 85.2 times as much carbon dioxide as hydrogen, and at 20° C., 49 times as much. A system has been devised on this principle for the manufacture of hydrogen from water gas at a cost of 3.0 Pf. per cubic meter. A product containing 99 per cent hydrogen can be prepared at a cost of 6.4 Pf. per cubic meter.

**Curme §** provides a method for the separation of various gases in a gaseous mixture containing acetylene, ethylene, methane and hydrogen with traces of other gaseous substances, such as impurities, whereby the available gases are separated one from another in a form and condition in which they are available for commercial use.

In carrying out the process, an apparatus as shown in Fig. 87b is filled with charcoal and connected with the container in which the body of gas is stored. The upper

\* German Patent No. 290,126, Feb. 7, 1914; J. S. C. I., 1916, 486.

† U. S. Patent No. 1,174,631; Chem. Abs., 1916, 1424, J. S. C. I., 1916, 527.

‡ German Patent No. 295,463, Apr. 15, 1913; J. S. C. I., 1917, 330.

§ U. S. Patent No. 1,181,116, May 2, 1916; J. S. C. I., 1916, 683.

pipes are connected to the receivers arranged to receive the respective gases. The charcoal, having an affinity for the acetylene and ethylene, is stated to take up or absorb these gases, while hydrogen and other gases pass through the vessel unchanged. This operation continues until the charcoal has taken up all of the acetylene and ethylene gases, which such a quantity of charcoal is capable of containing. Heat is then applied to the vessel, raising its temperature to around 200° C., at which

temperature all of the acetylene and ethylene contained in the charcoal will be driven out. When these gases have been completely expelled from the charcoal the latter is cooled and is ready for another operation. The hydrogen obtained is claimed to be free from all impurities of the type known as catalytic "poisons" so that it is considered especially well adapted for use in catalytic hydrogenation processes.

Scholl \* produces a mixture of nitrogen and hydrogen in which the ratio of nitrogen to hydrogen is equal to  $R$ , by mixing ammonia gas and air in the proportion of  $(2R + 4)$  to  $3R - 1$  and passing the mixture over a catalytic agent to induce dissociation of the ammonia and combination of the oxygen with hydrogen. For example, a mixture of equal parts of nitrogen and hydrogen is obtained by charging a closed vessel with ammonia gas under pressure, introducing air until the total pressure is four times the absolute pressure of the ammonia, and then passing the mixture over a catalytic agent.

An apparatus is described by Oyobigawa † whereby air-free hydrogen may be generated from the start, the waste solution may be discharged without admission of air, and the quantity of solid reagent may be regulated to control the pressure and volume of the gas.

The method of Quentin and Guillien ‡ depends upon the decomposition of water by fused zinc, the bath of zinc being kept molten by the combustion of a portion of the gas produced by the reaction. The apparatus consists of a bath for the molten zinc, in which is a perforated steam-coil connected with an outer coil heated by a burner. At the top of the bath an inclined surface is fixed, which carries the zinc oxide away as it forms.

A method for preparing hydrogen is described by Helbig § which is based on the reaction of aluminum with caustic soda; 810 g. aluminum and 3600 g. caustic soda are required to furnish one cubic meter of hydrogen. Inasmuch as commercial aluminum and caustic soda may be regarded as 99 and 77 per cent pure, respectively, 5485 g. of the latter would be required to furnish 1000 l. of hydrogen gas. Helbig notes that this yield constitutes a saving of 20 per cent as compared with the usual method based on the reaction of iron and sulphuric acid.

Activation of the aluminum is secured under the influence of heat, which brings about a considerable increase in the yield of hydrogen obtained when the product is subsequently treated with water.||

The activation of the aluminum results from the surface amalgamation of the metal, principally upon the production of the amalgam by the reduction of the

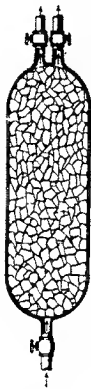


FIG. 87b.

\* U. S. Patent No. 1,123,394, Jan. 5, 1915; J. S. C. I., 1915, 228.

† Japanese Patent No. 29,910, August 18, 1916; Chem. Abs., 1917, 412.

‡ French Patent No. 476,994, May 18, 1914; J. S. C. I., 1916, 601.

§ Ph. praxis; through Boll. chim. farm., 53, 71, 1914; Chem. Abs., 1915, 1373.

|| German Patent No. 294,910, Jan. 27, 1916; L. Elkan Erben G.m.b.H., J. S. C. I., 1916, 386; Chem. Abs., 1918, 605.

mercury compound, and from the etching action of caustic soda. The amount of hydrogen evolved is claimed to be greatly increased if the activation is effected in whole or in part with heating, either amalgamating the aluminum with heating, or etching with caustic soda in the heat, or carrying out the whole process at an elevated temperature. In the subsequent evolution of hydrogen the use of hot water is not then necessary, e.g., 50 g. aluminum filings are heated on the sand bath in a dish for about thirty minutes at  $180^{\circ}$ , and then sprinkled with 1 per cent mercuric chloride solution. The excess is poured off and washed with pure alcohol. After drying 0.2 g. of the product are drenched with about 10 cc. of a 1 per cent caustic soda solution which, after a short time, is made up to 1 l. with pure water. In twenty-five minutes about 40 cc. hydrogen are evolved. Without previous heating of the aluminum, only 31 cc. hydrogen are evolved under otherwise like conditions.

According to Hamlin \* balloons are generally inflated with hydrogen from scrap iron and hot acid, unless there is some other source of the gas close at hand. The French army has made use of processes which would be far too expensive for most commercial purposes, but which have the advantage of requiring none but readily portable materials and apparatus.† Simple apparatus designed by Jaubert for the decomposition of "hydrolith," which is essentially calcium hydride with some calcium oxide and nitride, yields 1 cubic meter of hydrogen per kilogram of hydrolith. Jaubert's process involving the treatment of ferro-silicon or manganese-silicon with water and caustic soda appears to be a reaction difficult to control. Jaubert has, therefore, introduced another "hydrogenite" process. Ferro-silicon is intimately mixed with dry caustic soda and quicklime, and the bricks obtained are sealed in tin cases to keep out moisture. When wanted, the brick is placed within a water-jacketed apparatus, and a hot wire is forced into the brick. The mass burns without giving any flame, some steam is generated in the jacket, and this steam enters the brick and hastens the liberation of hydrogen. The ferro-silicon used is of a very high grade, containing more than 90 per cent of silicon. The reactions give hydrogen, lime and sodium silicate; the iron is unessential, and is used only because it is cheaper to manufacture rich ferro-silicon than to isolate silicon itself.

Fourniols ‡ gives a review of the methods that have been proposed for the commercial production of hydrogen. The hydrogenite, hydrolith, and silicol processes are discussed at some length with reference to apparatus for field use.

He states that the problem of transportation presents the greatest difficulties in connection with the utilization of the hydrogen gas set free in large quantities as a by-product in electrolytic caustic and chlorine plants. In transporting this hydrogen the great weight of the cylinders which must be moved to get a small amount of hydrogen to a certain point was a serious obstacle. This gave rise to the development of the other processes above mentioned involving the use of portable generating apparatus. A comparison of the price of transportation in this way with the compressed hydrogen method is given as follows:

\* J. Ind. and Eng. Chem., 1915, 542.

† Engineering, 99, 1915, 415.

‡ Rev. gen. sci., 1915, 26, 339; Chem. Abs., 1915, 2294.

<i>Cylinders with Compressed Hydrogen</i>		<i>Hydrolith</i>	
	Francs		Francs
8000 tubes at 80 fr. ....	640,000	48 tons at 5 fr. per kg. ....	240,000
50,000 cubic meters of hydrogen at 0.40 fr. ....	20,000	Apparatus for generating. ....	40,000
Carriers for tubes. ....	60,000	Carriers for reagents. ....	4,000
12 carriages of 3 tons. ....	240,000	2 carriages of 3 tons. ....	40,000
	<hr/> 960,000		<hr/> 324,000

This table is only intended to compare transportation cost. The hydrolith process is expensive as a stationary means of production. Fourniols states that the latest German process for both lighting and inflating purposes, using coke and oil, is also capable of being transported ready for generating purposes.

Barnitz has reviewed the field of hydrogen production and utilization in Metallurgical and Chemical Engineering, April 1, 1916 and Journal of the Aeronautical Society of America, May-June, 1916. In the first-mentioned paper the Linde process, iron and steam method, hydrogen by the decomposition of hydrocarbons and by electrolytic methods are considered. The application of hydrogen in the hydrogenation of fatty oils is briefly discussed. Modern methods of manufacture of hydrogen are outlined by Gas World, 1918, 68, 4. In the report of the British Comptroller and Auditor General, it is stated, that the cost of hydrogen gas showed an increase from \$4.60 per 1000 cu. ft. in 1912-13 to \$5.25 in 1913-14.\* The output during the latter year was 2,023,607 cu. ft. as compared with 3,493,296 cu. ft. in 1912-13. Seeker † outlines the methods in use for the commercial production of hydrogen and the manner in which the gas is employed for industrial purposes. The generation of hydrogen by different methods and the cost of equipment is discussed by Bontoux.‡ A review of the developments in hydrogen gas manufacture during 1914 appears in Zeitsch. angew. Chem., Aufsatzteil, 1915, 221. Sander § gives a review of the principal processes for the manufacture of hydrogen on the large scale for military purposes; and of the methods for handling the gas in the field. A review of the subject of the application of hydrogen gas in aeronautics is given by Redgrove.|| The production of hydrogen by the electrical decomposition of acetylene, the use of hydrolith, hydrogenite and the like are discussed. The manufacture of hydrogen for military purposes is ably described by Ardery.¶

Crossley\*\* discusses at length the methods of manufacture of hydrogen and its uses. A review of modern apparatus for the preparation of hydrogen is given by Kausch.††

Teissier and Chaillaux ‡‡ heat a mixture of barium sulphate and

\* J. Gas Lighting, 129, 1915, 442.

† Polytech. England, 1914, 61, 66; Chem. Abs., 1914, 3619.

‡ Matières Grasses, 1914, 4194; Seifen. Ztg., 1914, 987.

§ Chem. Abs., 1916, 808, J. Gasbel, 1915, 637.

|| Chem. Trade J., 60, 359; Chem. Abs., 1917, 2264.

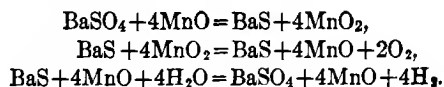
¶ Trans. Am. Electrochem. Soc., 1916, 29, 549; Met. Chem. Eng., 1916, 14, 333.

\*\* J. S. C. I., 1914, 1135.

†† Berlin Chem. App., 1915, 2, 125 and 141.

‡‡ French Patent No. 447,688. 1912: J. S. C. I., 1913, 234 and 1914, 1137.

manganous oxide to a red heat, finally to a white heat, and pass steam under pressure over the resulting mass, when the following reactions are stated to take place:



## CHAPTER XXVI

### HYDROGEN BY THE ELECTROLYSIS OF WATER

The production of hydrogen and oxygen by the electrolysis of water, though one of the oldest electrochemical experiments, and proposed in a large number of patents, in the past has been carried out industrially only to a limited extent. There was considerable difficulty in developing the laboratory apparatus so that it would operate successfully in practice, one of the hardest conditions to meet being the necessity of absolute safety of operation, and this required the exclusion of every possibility of the formation of an explosive gas mixture. Another difficult matter was the requirement of providing a material for the electrodes, which was not at all or only slightly attacked by the electrolyte, and the necessity of constructing apparatus with a small internal resistance.\*

These problems appear now to have been worked out satisfactorily so that large scale electrolysis of water is on a solid industrial basis. The principal processes or systems used in practice include those of the International Oxygen Co., Garuti, Schoop, Siemens-Halske, Schmidt, Schuckert and Burdett.†

\* The Electrolysis of Water, Richards and Landis, Trans. Am. Electrochem. Soc., III, 104, and IV, 112, is concerned largely with the theory of the subject, while a paper by Richards bearing the same title, appearing in the Journal of the Franklin Institute, 1905, 377, treats of practical developments in hydrogen and oxygen generation.

† In the electrolysis of water there are certain constants whose values are the same under all conditions of operation within certain limits. The *first* constant is the amount of hydrogen liberated per ampere hour of current passed through the cell generator; the figure is 0.03738 gram or 0.014825 cubic foot of hydrogen gas measured at 0 degree and 760 mm. pressure. Thus, at 400 amperes, which is the customary operating amperage for most cell generators, the production will be 5.93 cubic feet of hydrogen and 2.96 cubic feet of oxygen (at 0 degree and 760 mm. pressure) per hour. At 20 degrees and 760 mm. pressure the output will be 6.36 cubic feet of hydrogen and 3.16 cubic feet of oxygen per hour per cell generator. The *second* constant is the minimum voltage that will force the current through the cell generators. For a solution of sodium hydroxide in water the minimum voltage is 1.69 volts, for potassium hydroxide 1.67 volts; this, then, is the lowest voltage at which decomposition of water, or electrolysis, takes place. In order to produce gas with current at this voltage, the cell generator would have to be constructed in such a manner as to do away with all internal electrical resistance which is obviously impossible and so the operative or practical voltage is higher than the theoretical. With a current of 400 amperes the voltage will vary from 1.9 to 4, depending

D'Arsonval, in 1885, was perhaps the first to install a plant for furnishing oxygen electrically in the laboratory. He used 30 per cent caustic soda solution as electrolyte, cylindrical sheet-iron electrodes, a current density of two amperes per square decimeter, and enclosed the anode in a woolen bag, to serve as a diaphragm. Only the oxygen was saved. The apparatus used sixty amperes, furnished some 100 to 150 liters of oxygen daily, and was in use several years.

Latchinoff used an asbestos cloth partition, ten per cent caustic soda solution, iron electrodes, 3.5 amperes per square decimeter and 2.5 volts working tension; or with a five to fifteen per cent sulfuric acid solution he used lead anodes and carbon cathodes. In his first apparatus, Figs. 88 and 89, the units were all in parallel, but afterwards he used series electrodes, the one side of an electrode acting as an anode and the other as a cathode; a series of forty was

on the type of cell generator. With the first constant given the amount of hydrogen produced per 400 amperes per hour and the minimum or theoretical voltage given it is a simple matter to determine the yield of gas per kilowatt-hour of electricity used. The theoretical efficiency will be 400 amperes  $\times$  1.69 volts or 0.676 kilowatt-hour to produce 6.36 cubic feet of hydrogen. The theoretical yield per kilowatt-hour per cell generator will be 9.408 cubic feet of hydrogen. In practice the yield is from 4.5 to 8.25 cubic feet of hydrogen per kilowatt-hour.

In general, electrolytic plants consist of the following important parts, cell generators for producing the gases, a motor-generator set to deliver a direct current at the proper potential or voltage, gasometers and storage tanks for storing the gas as it is generated and compressors and compressor motors for raising the pressure of the gas to the required point. Stripped of everything but essentials the component parts of all cell generators are: a container tank for holding the solution; one or more positive electrodes, one or more negative electrodes, immersed in the solution; means for separating the electrodes to prevent mixture of gas and means for separately collecting the gas as it is generated. The separating medium is usually a diaphragm and may be of metal, earthenware or cloth. The diaphragm may be a conductor or non-conductor of electricity and if of conductive material it should be insulated from the electrodes. The effect of the diaphragm is to divide the generator into two or more partitions, and the gases as generated will rise to the top of the partition, there to be drawn off by means of pipes which lead to header pipes connecting a line of cell generators, each gas, of course, being drawn off by means of separate pipe lines. The header pipes in turn are connected to a main gas line which leads the gases to their respective gasometers. From the gasometers the gas is drawn off by means of compressors and compressed into storage tanks for use.

The majority of installations require a motor-generator set to obtain the required voltage for operating. The current must be direct. The motor-generator set should be heavily built in order to operate on a twenty-four hour load. The compressors employed are specially adapted for handling these gases. The size and character of the gasometers used, of course, depends on the size of the installation.

Below is given a typical operating cost of an electrolytic plant consisting of 100 cell generators with a production capacity of 632 cubic feet of hydrogen and 316 cubic feet of oxygen in one hour and 15,168 cubic feet of hydrogen and 7584 cubic



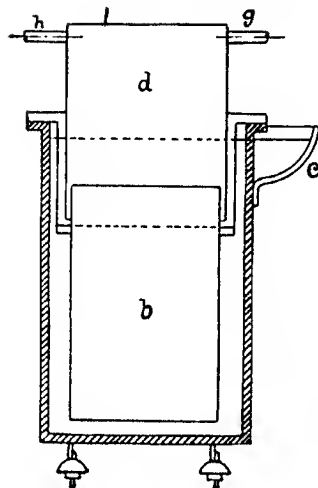


FIG. 88.

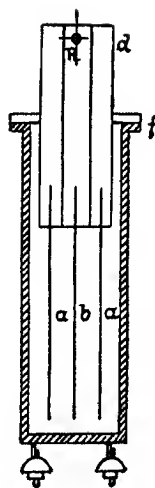


FIG. 89.

feet of oxygen in 24 hours. The yearly production, 300 days 24 hours per day, is 4,550,400 cubic feet of hydrogen and 2,275,200 cubic feet of oxygen.

Each cell generator requires about 2 volts at 400 amperes equivalent to 800 watts or 0.8 kilowatt-hour.

100 cells  $\times$  0.8 K.W.H.  $\times$  24 hours  $\times$  300 days = 576,000 K.W.H. yearly plus 25 per cent for loss through motor-generator set = 720,000 K.W.H. yearly.

Hydrogen compression requires 4 K.W.H. per hour.

4 K.W.H.  $\times$  24 hours  $\times$  300 days = 28,800 K.W.H. yearly.

(Compression to 300 pounds per square inch.)

Oxygen compression requires 12 K.W.H. per hour.

12 K.W.H.  $\times$  24 hours  $\times$  300 days = 86,400 K.W.H. yearly.

(Compression to 1800 pounds per square inch.)

Current consumption yearly:

Cell generators.....	720,000
Hydrogen compression.....	28,800
Oxygen compression.....	86,400
Total.....	835,200

Fixed charges:

Depreciation, maintenance, yearly.....	\$3000.00
Interest on investment.....	1500.00

Labor:

300 days, 24 hours, at 30 cents per hour.....	\$2160.00
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With current at a price of say 1 cent per kw.-hour, which although a low rate is not excessively low for this class of service, the total operating cost will be \$15,012.00 per year.

The demand for oxygen in metal working lines is at present so great and so poorly met that in the majority of cases the oxygen produced by an electrolytic plant may be disposed of under contract at such terms as will result in the hydrogen being produced at a relatively low cost.

used on a normal lighting circuit, with current density of ten amperes per square decimeter, and parchment partitions between the electrodes to separate the gases. Latchinoff was also the first to carry out the decomposition under pressure, using a strong iron vessel as electrolyzer, and by an ingenious system of floating valves keeping the pressure of the two gases equal in the apparatus. Fig. 90 shows this apparatus, the action of which will be evident from a short inspection.

Renard's apparatus for the generation of hydrogen is shown in Fig. 91. The container is made of cast iron and serves as the nega-

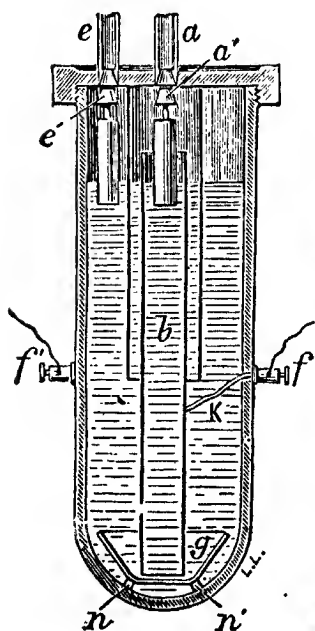


FIG. 90.

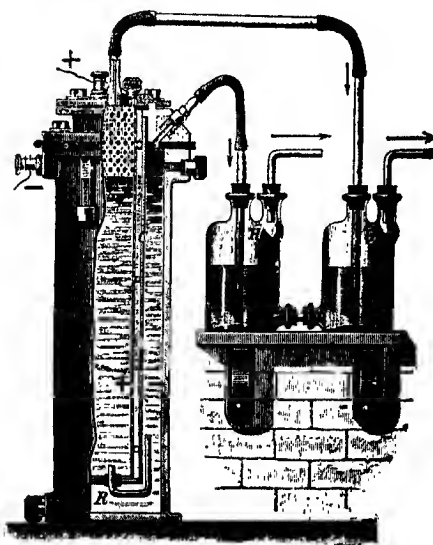


FIG. 91.

tive electrode. The cylinder *C* of asbestos material encloses the positive electrode which is cylindrical in shape and is made either of iron or nickel. Through the bottom of the diaphragm cylinder the U-tube *R* establishes communication between the inner and outer vessels. The electrolyte is a solution made by dissolving 15 parts

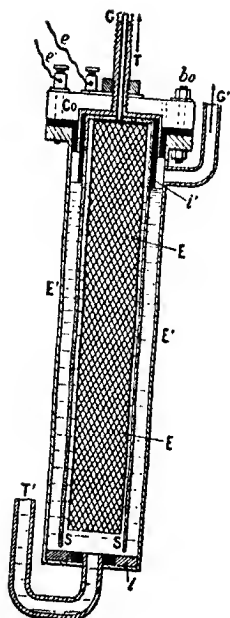


FIG. 92.

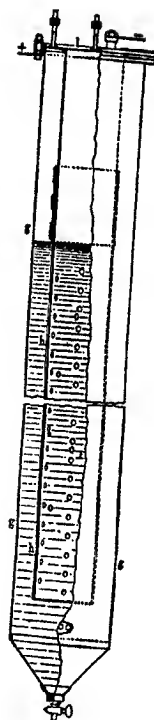


FIG. 93.

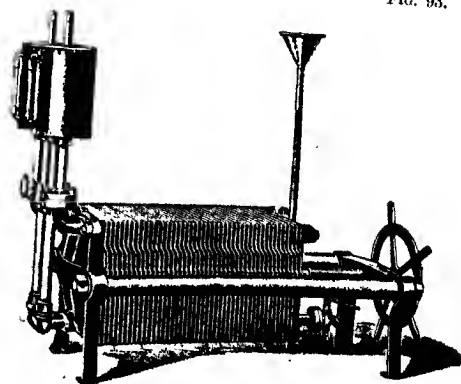


FIG. 94.

of caustic soda in 100 parts of water. Before the gases are passed to the gas holder they are led through the pressure equalizer marked *H* and *O*. With a current of 25 amperes at 3.5 volts a yield of 12 liters of hydrogen and 6 liters of oxygen per hour is obtained.

A form of construction of the Renard \* type is shown in Fig. 92 and also in Fig. 93.

The multiple cell of Schmidt † looks somewhat like a filter press, Fig. 94, and consists essentially of bipolar, iron electrodes, connected in series. Each frame in the press contains an iron electrode, which acts as a double-pole (bipolar) electrode, sheets of asbestos cloth held between the frames acting as partitions, reinforced with rubber on the edges for making tight joints. The electrolyte is a ten per cent solution of potassium carbonate, filled into the apparatus through the standpipe on the right, which communicates with all the compartments through holes in the frames similar to the usual filter-press construction. The gases evolved escape by similar passages into the cylinders on the left end, where they separate from the electrolyte and pass upwards, while

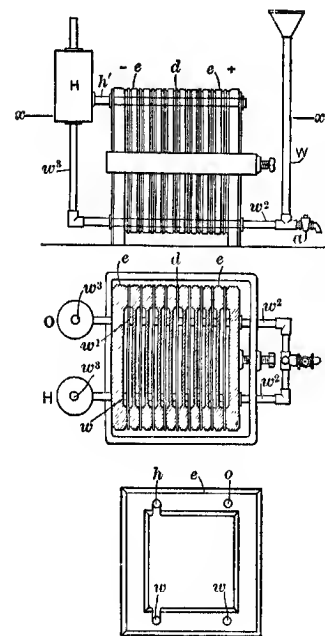


FIG. 95.

the electrolyte, dragged by the gas bubbles, flows downwards back into the apparatus, thus maintaining an efficient circulation. With forty plates about 2.5 volts are absorbed in each cell, using a current density of about two amperes per square decimeter.‡

The apparatus is shown in detail in Fig. 95. A 110-volt direct-current lighting circuit may be employed for the operation of a series type apparatus composed of the requisite number of cells. The press

\* Delmard, German Patent 58,282, Nov. 23, 1890.

† German Patent 111,131, June 13, 1899.

‡ A multiple-cell generator of the filter press type is manufactured by Shriver & Co., Harrison, N. J.

A filter-press type of hydrogen generator having an output of 16 cu. m. of hydrogen per hour is made by Maschinenfabrik Sürth, G.m.b.h. Sürth am Rhein bei Köln.



FIG. 96. Shriver oxy-hydrogen generator.

has to be taken apart and cleaned every six weeks and the asbestos diaphragms have to be renewed from time to time.

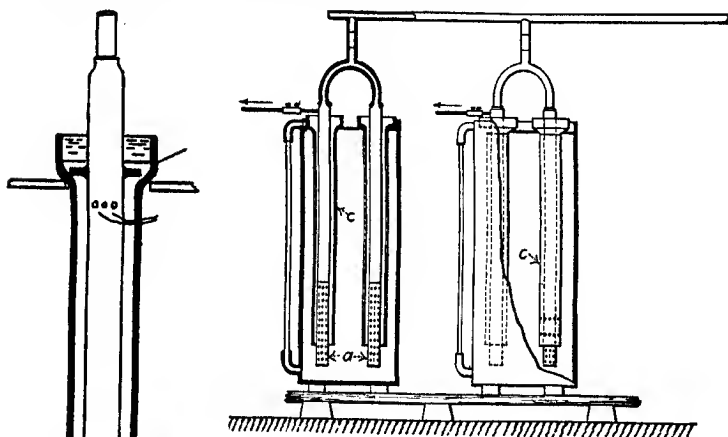


FIG. 97.



FIG. 98.

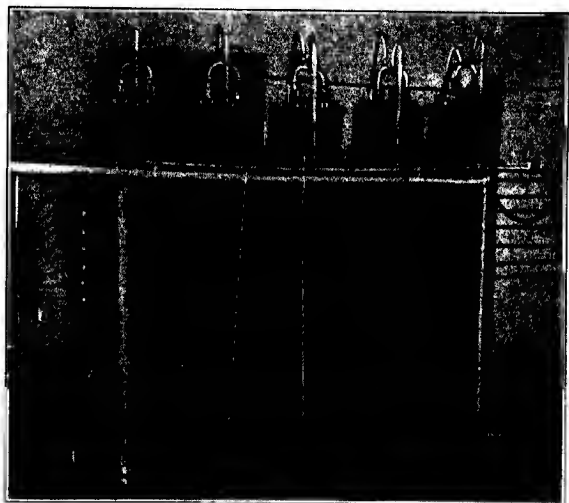
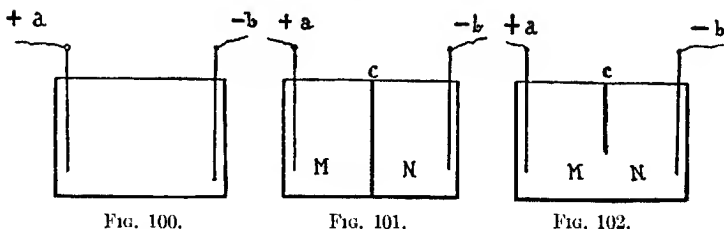


FIG. 99.

Schoop, in 1900, devised an apparatus with non-conducting and non-porous partitions, which has gone into considerable commercial use. Fig. 97 shows the section of the apparatus, where *aa* are the

tubular electrodes of sheet hard lead, enclosed by glass or clay suspended tubes *c*, which are perforated at their lower end; the electrode surface is further increased by fine hard lead or iron wires hung inside the tubular electrodes, the latter being perforated above the level of the electrolyte in order to let the internally-generated gas escape. Each cylinder contains two anodes and two cathodes. When alkaline electrolytes are used and iron electrodes, the working voltage is 2.25; when sulfuric acid of density 1.235 is used, with hard-lead electrodes, the working voltage is 3.6 to 3.9. Fig. 98 shows a single electrode and Fig. 99 an installation of the Schoop system.\*



Garuti, in 1892, introduced a new electrolytic principle into these apparatus for the decomposition of water. He used a nearly complete metallic partition between the electrodes, and avoided the evolution of gases on this partition by keeping the working voltage between the electrodes below three volts. A metallic partition can only act as an intermediate or bipolar electrode by virtue of the current entering and leaving it; but this would make two decompositions between

\* Schoop (Zeits. Elektrotechn. Wien (1900), 18, 441) discusses the difficulties met with in the construction of a suitable apparatus for the technical electrolytic manufacture of hydrogen and oxygen, and gives a description of patents dealing with this subject. In the Schoop apparatus it is claimed that 1.5 cubic meters of hydrogen and oxygen are produced per 11 horse-power hours. Richards (Jour. Franklin Inst. (1905), 390) notes that the output is given as 68 liters of oxygen and 136 liters of hydrogen per electrical horse-power hour. A description of the Schoop system is given in the *Centralblatt f. Accum.*, Feb. 15, 1903. It is stated that the length of the tubes is chosen according to the pressure under which the gases are wanted. The following results were obtained with the Schoop apparatus during one year: One electric horse-power hour gives 97.5 liters of hydrogen and 48.75 oxygen (probably under atmospheric pressure); i.e., for one cubic meter of mixed gas 6.8 horse-power hours are required; with warm acid (sulfuric acid of 1.23 specific gravity being always used) this value is reduced to 6.2 horse-power hours; if the price of one horse-power is 1 cent, the cost of the production of one cubic meter of mixed gases is 4.2 to 4.8 cents. The purity of the oxygen is 99 per cent, that of the hydrogen 97.5 to 98 per cent.

the original electrodes, necessitating an absorption of  $2 \times 1.5 = 3$  volts in decomposition. As long as the working voltage is kept below 3, the partition must act merely as a partition, the same as a non-conducting partition. Reference to Figs. 100, 101 and 102 will make this entirely clear. If 2 electrodes are placed in a vessel (Fig. 100)

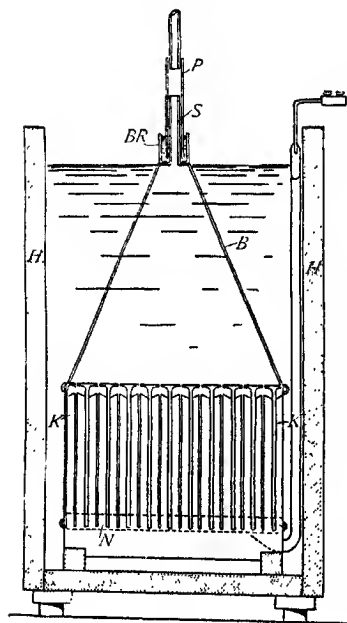


FIG. 103.

metal instead of burnt clay, rubber, glass, etc.

Garuti devised many modifications in the details of his cells, of which Fig. 103 may represent the most recent. The original forms made of sheet lead (using dilute sulfuric acid electrolyte) got out of shape too easily, and were replaced by sheet-iron apparatus, using caustic soda solution. The electrodes are only twelve millimeters from each other, and separated by a sheet-iron partition with small perforations in it, the latter allowing free passage of current but being too small to allow any gas bubbles to pass. The alternate compartments are connected with oxygen and hydrogen mains, in which are enlargements for collection of spray and moisture, which runs back into the cell. Current densities of two to three amperes per square decimeter are possible with a working voltage between 2.45 and 3,

containing acidulated water and are separated by a sheet of metal *c* (Fig. 101), two separate decomposition chambers result and the sheet metal serves as a bipolar electrode, so that the side towards the anode evolves hydrogen and that towards the cathode, oxygen. Since the 1.5 volts are required for the decomposition of water, the cells *M* and *N* will require 3 volts. If the diaphragm is raised somewhat so the chambers *M* and *N* are in communication (Fig. 102) the evolution of gas will take place only on the terminal electrodes and not on the intermediate conducting septum. The latter becomes a bipolar electrode only when the electromotive force exceeds 3 volts. The advantage gained by the Garuti process is in the simplicity and economy of making the partitions of sheet



using caustic soda solution of 21° Bé. The cell shown in Fig. 104 is intended to take 400 amperes, and to require one kilowatt of power.

The Garuti type C11 generator consists of 45 separate compart-

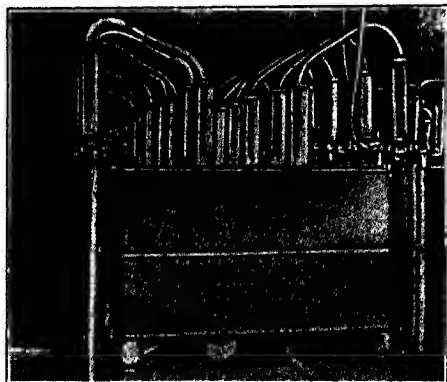


FIG. 104.

ments made of 16-gauge sheet iron welded together to form a single unit.\* The sides of the compartments are used as diaphragms and are usually perforated (Fig. 105) to allow circulation of the electrolyte but

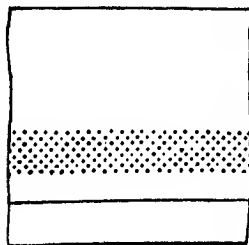


FIG. 105.

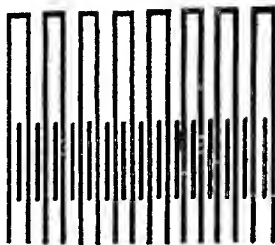


FIG. 106.

Perforated compartment walls of the Garuti generator.

\* In 1892 Garuti took out a patent (British Patent 16,588, April 25, 1892) describing an apparatus consisting of a container having an inverted leaden case with partitions of sheet lead soldered together so as to form a case divided into parallel cells open only to the water at the bottom. The partitions of the cells separate the anodes and cathodes which are placed alternately and are insulated in the cells by means of combs made of suitable material. In 1896 Garuti and Pompili (British Patent 23,663, Oct. 24, 1896) described an improvement on the former patent, involving the perforation of the diaphragms in their lower part by small holes as near as possible to each other. See also U. S. Patents to Garuti 534,259, Feb. 19, 1895, and Garuti and Pompili 629,070, July 18, 1899.

not the gas. The perforations extend lengthwise along the lower edge of each compartment wall 3 inches from the bottom, forming a

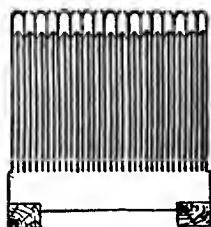


FIG. 107. Compartments of the Garuti generator.

perforate strip  $2\frac{1}{2}$  inches wide. An electrode is placed in each compartment and the electrodes are alternately positive and negative. All like electrodes are connected together. Each compartment is  $\frac{3}{4}$  inch in width and 30 inches long. The electrodes are insulated from the compartments and are prevented from coming in contact with the walls by means of small porcelain insulators. The gas from all of the hydrogen-producing compartments is collected in a gas bell welded to one side of the cell proper

and is led through a water seal and to a header pipe and then to a gasometer. The oxygen gas is handled in a like manner. The cells as well as the container tanks and pipe lines are insulated from the ground. The pipe from the cell to the header pipe is insulated from the latter by means of a sleeve of rubber and glass.\*

Siemens Bros. & Co. and Obach devised the apparatus shown in Fig. 112, the principle being similar to that of the Garuti. The cast-iron vessel *a* is surrounded by heat-retaining material, in order that the temperature of the cell may be automatically raised and thus its running resistance lowered. A cylindrical iron anode *f* is separated from the encircling cathode *g* by a cylinder of wire netting *c*, held in place by the porcelain block *k*. The electrolyte is dilute caustic soda; the gases escape above from the spaces *n* and *m*. The whole

\* When the Garuti cell is first installed the efficiency will often be as high as 6 cubic feet or so of hydrogen per kw.-hour, but the depreciation is said to be perhaps more rapid than in some other types of generators and in time the hydrogen output may drop to about 5 cubic feet. Thus under the normal operating amperage of 350 or 400, from  $2\frac{1}{2}$  to 3 volts per cell will be required. The rather rapid depreciation of the generator is said to have held back its use to some extent. Owing to the lightness of the materials employed and also possibly because of insufficient electrode surface, the anode is liable to be attacked and eventually worn away. The minute particles of iron or iron compounds formed are said to have a tendency to be deposited on the cathode. The insulators, employed to prevent the contact of electrode with the compartment wall, form a convenient place of deposit for the iron particles with possible danger of causing a short circuit between the electrode and the compartment walls. If one compartment is short circuited the entire cell becomes "shorted" and this short circuit will cause the generation of mixed gas. The entire cell should be dismantled about once a year and cleaned with either a stream of water or by means of a sand blast.

The American Oxhydric Company, Milwaukee, Wis., have had generators of the Garuti type in operation for several years.

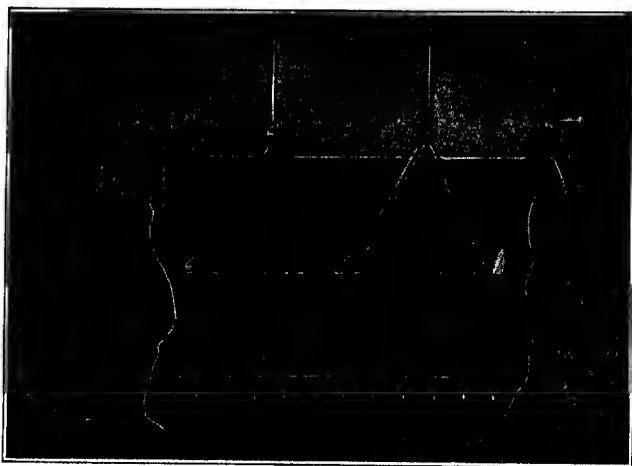


FIG. 108. Garuti generator.

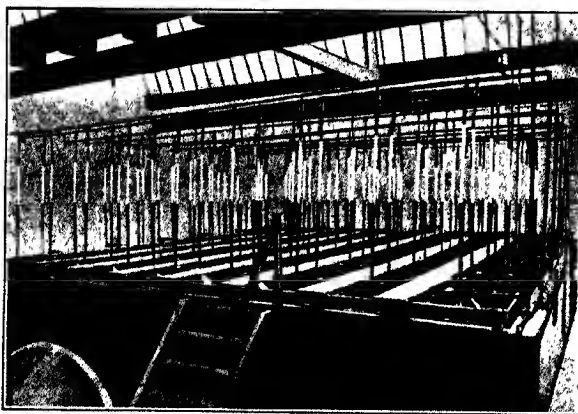


FIG. 109. Battery of Garuti generators.

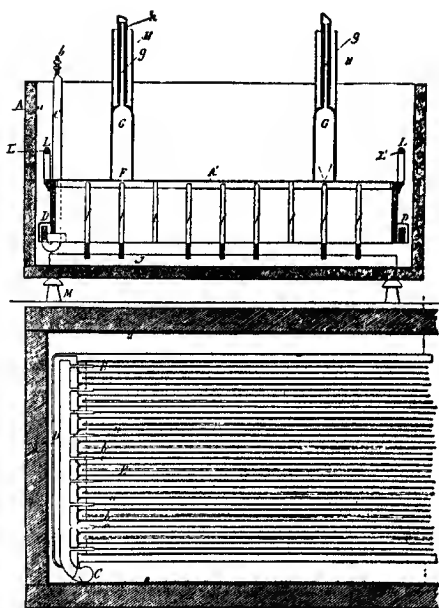


FIG. 110. One form of the Garuti generator.

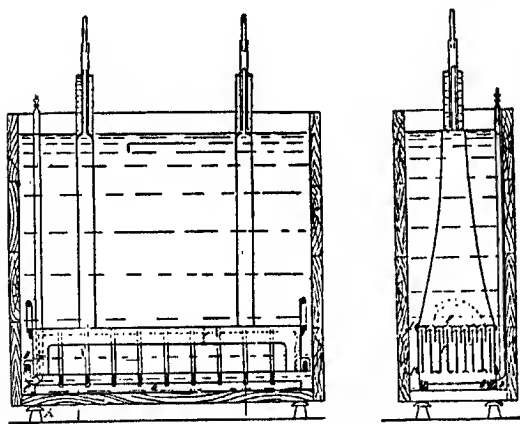


FIG. 111. A modified form of the Garuti generator.

apparatus is set on insulating porcelain feet. The normal type of apparatus is built to take 750 amperes at 3 volts drop of potential, and furnishing eleven cubic meters of oxygen and twenty-two cubic meters of hydrogen per twenty-four hours, using up 162 kilowatt-hours.\*

Fiersot describes† an apparatus of Siemens and Halske for the electrolysis of water in which a 10 per cent

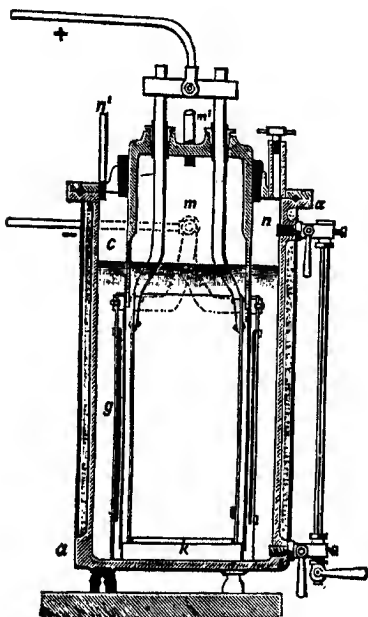


FIG. 112.

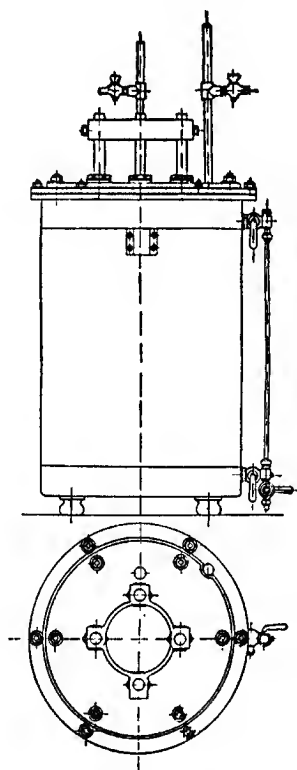


FIG. 113. Plan and elevation of Siemens Bros. and Obach generator.

solution of potassium carbonate is used as electrolyte. One hundred and thirty-four grams of water are decomposed per kilowatt-hour. By heating the electrolyte the output may be increased by 8 per cent. The electrolytic oxygen thus produced is on the average 97 per cent. pure, while the hydrogen contains one per cent of oxygen.

Another form of metallic diaphragm cell has been devised by Fischer, Luening and Collins.‡ The generator consists of a tank

\* Jour. Franklin Inst. (1905), 392.

† Electrochemical Ind. (1904), 28.

‡ U. S. Patent 1,004,249, Sept. 26, 1911.

containing an electrolyte in which an indifferent number of independent, preferably oblong, metallic cases are submerged. An illustration of the case is shown in Fig. 114. The case is open at the bottom and is divided into a pair of cells by a metallic diaphragm. Electrical connections to the anode and cathode and exit pipes situated on the upper side of the case are provided for the removal of the gases.

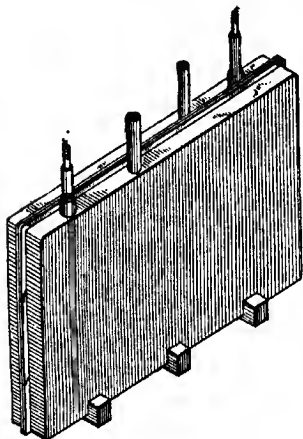


FIG. 114.

The apparatus of the **Schuckert** system \* is constructed, with the exception of the copper feed wires and the insulating material, entirely of iron. The cell proper of a unit designed to accommodate 600 amperes consists of a cast-iron trough (Fig. 115), approximately twenty-six inches long by eighteen wide and fourteen deep, requiring, when in operation, about 50 liters of electrolyte. In this trough are placed the iron electrodes. These are separated by strips of a good insulating material, extending from the top downward about three-

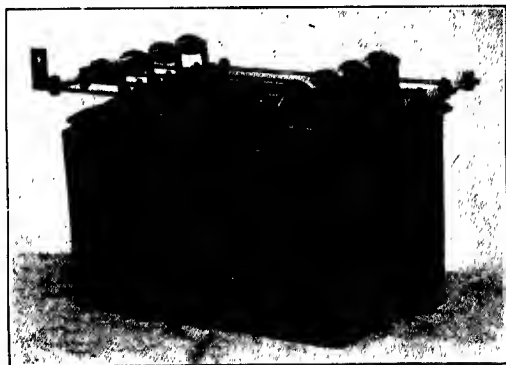


FIG. 115. Schuckert cell.

fourths the depth of the cell. Between these separating plates and enclosing the electrodes are suspended iron bells, which collect and carry off the gas there generated. The electrolyte is usually a 20 per

\* Electrochem. Ind. (1903), 579.

cent aqueous solution of pure sodium hydrate, although a 15 per cent solution may be used. The concentration is maintained by supplying to the cells an amount of distilled water equal to that decomposed and carried away mechanically by the gas. The loss of sodium hydrate

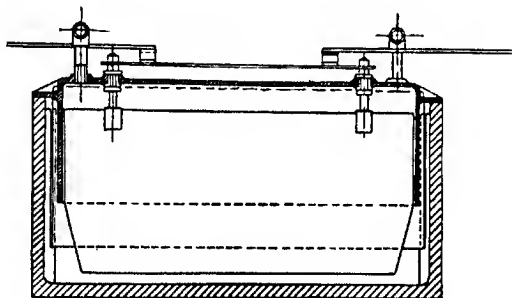


FIG. 116. Longitudinal section of Schuckert cell.

is inappreciable and may be entirely eliminated if the first wash water be used as feed water for the cells. The units may be connected either in series or parallel with a drop of potential between electrodes of from two and one-half and three volts. The apparatus is operated

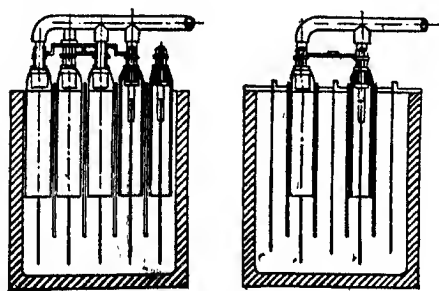


FIG. 117. Cross section of Schuckert cell.

most economically at a temperature of 70° C. When the cells are protected from radiation, as can be done, for example, by placing them on wooden boxes and packing them in one or two inches of sand, the heating effect of the passing current is sufficient.\*

\* The Elektrizitäts-A.G. Vorn. Schuckert & Co. have taken out German Patent 231,545, Aug. 13, 1910, for the addition of soaps or soap-forming substances, preferably emulsified soaps, and of ferric oxide to the alkaline electrolyte employed.



FIG. 118.

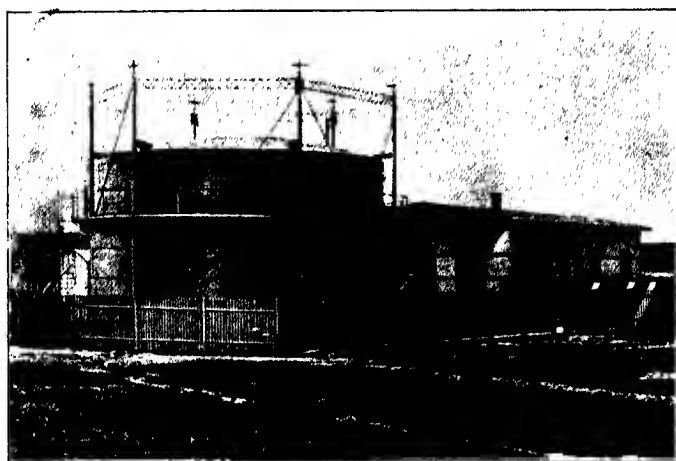


FIG. 119.



The standard types of apparatus are designed to take from 100 to 1000 amperes, and to furnish gas at a pressure equal to a water column of 70 to 80 mm. For special purposes a cell delivering gas sustaining a water column of 760 mm. may be secured. The production of normal types of apparatus is about 150 liters of hydrogen and 75 liters of oxygen per kilowatt-hour when measured over water at atmospheric pressure, and at 20° C. The attention required for a plant of this kind consists simply in supplying the requisite amount of water to maintain the concentration constant. When in continuous operation the positive electrode, which is made up of a sheet iron plate two millimeters thick, should be replaced at the end of each year.\*

Fig. 118 shows the interior of a plant furnishing 1200 cubic meters hydrogen daily. Fig. 119 shows the exterior of this plant. An equipment for an hourly production of 4 cubic meters hydrogen is shown in Fig. 120. Fig. 121 is a compression room for charging cylinders with oxygen at 150 atmospheres pressure.



FIG. 120.

A modified form of the Schuckert cell, as shown in Figs. 122 and 123, comprises a container tank, constructed of welded sheet iron and a number of positive and negative electrodes immersed in the solution. Eight separate bell castings are employed to house the electrodes and collect the gas as it is generated. These bell castings are made of a close-texture gray iron and are suspended from the top of the container tank by means of U-shaped steel supports. The container tank and the bell castings

\* See Sci. Am. Suppl. (1913), 363.

play no part in the operation of the generator and are insulated from the electrodes and all current-carrying metal. The electrodes are made of steel plates to each of which are welded two steel rods, both rods serving as terminals as well as supports for the electrode, holding it in position within the bell casting. The electrodes are alternately positive and negative. All of the positive electrodes are connected together by means of bus bars across the top of the tank and are led to a common terminal. The negative electrodes likewise are connected together and led to a common terminal. Each bell casting is tapped for an eduction pipe to draw off the gas as generated. The four hydrogen pipes are connected together as shown and are led to the hydrogen pipe line connecting a battery of generators. The oxygen pipes are connected likewise. The electrolyte fills the container and owing to its height above the electrodes the gas is generated under an appreciable pressure amounting to approximately one pound per square inch.

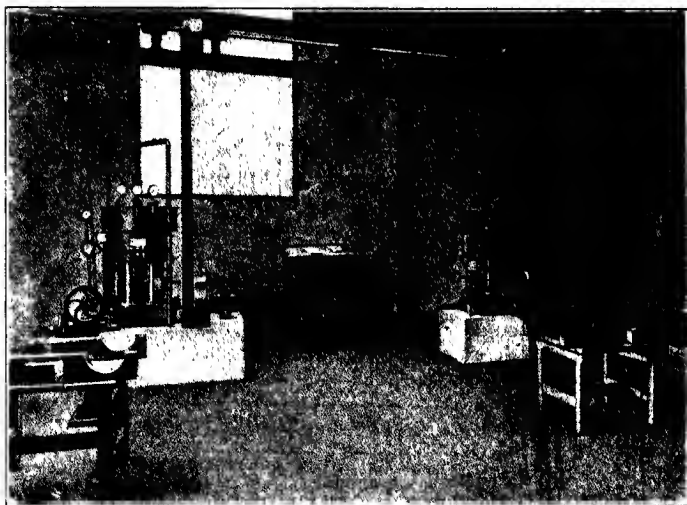


FIG. 121.

The novelty that distinguishes the Schuckert cell from the majority of other generators is the absence of any diaphragm in the construction. While a diaphragm is actually not used, still the sides of the bell castings act in the capacity of a diaphragm to prevent the mixing of the gases.

The working efficiency of the Schuckert cell under normal conditions of temperature is said to average from 4.5 to 5.5 cubic feet of hydrogen per kilowatt-hour of electricity passed through it. Or, in other words, the voltage required to force 400 to 600 amperes through each cell will vary from 2.9 to 3.5 according to the condition of the plant. The Schuckert generator was one of the earliest placed on the market and at the present time three plants of this type are reported in use in the United States. Too high an amperage results in so rapid an evolution of gas that there is

a tendency under these conditions for the gas in one chamber to be forced down and under the wall of the next partition which, of course, will result in mixed gas or the escape of gas into the generator room.

Another difficulty said to be met with in operating under high amperage is the wearing away of the anode, charging the electrolyte with small particles of iron compounds which show a tendency to be attracted to the cathode and gradually form a deposit. These accretions have been known to build across the space between the electrode and the bell castings causing short-circuiting and permitting the bell castings to become charged, with consequent evolution of gas on its outer side and the escape of gas into the generating room.\*

Details of construction of an electrolytic apparatus for the production of hydro-

\* The Schuckert apparatus is supplied by the Elektrizitäts-A-G. Vorm. Schuckert & Co., Nurnberg. In a private communication they state that an electrolyzer battery, capable, when running at a temperature of 50° to 60° C., of producing hourly 10 cubic meters of hydrogen, yields the gas of 99.5 per cent purity. For this equipment they quote:

Electrolyzer .....	\$2350
Caustic soda (containing a little chlorine and sulfur) 1450 kilos ..	410
Insulating material .....	100
2 scrubbers, driers, and safety devices, pressure regulators and gauges .....	250
2 gas-purifying stoves .....	500
Packing for over seas and freight .....	240
Total .....	\$3850

Other auxiliaries are:

2 gas holders (10 and 20 cubic meters) .....	\$2000
Wooden staging and boxes to contain the battery embedded in sand for protection against loss of heat .....	200
Compressors .....	2850
Water-distilling apparatus .....	200
Miscellaneous .....	525

The temperature of the electrolyzer room should be maintained at least at 15° C. In cold weather it must be heated.

An electrolytic hydrogen and oxygen generator of the bell-collector type is described by Benker (J. S. C. I., 1914, 256, and French Patent 461,981, Aug. 29, 1913).

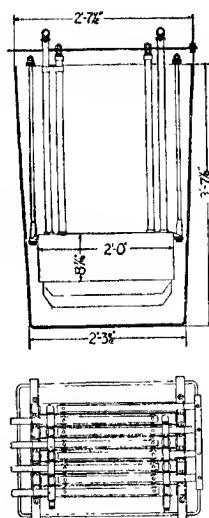


FIG. 122.

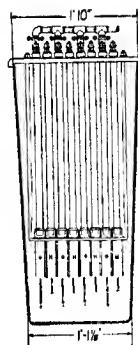


FIG. 123.

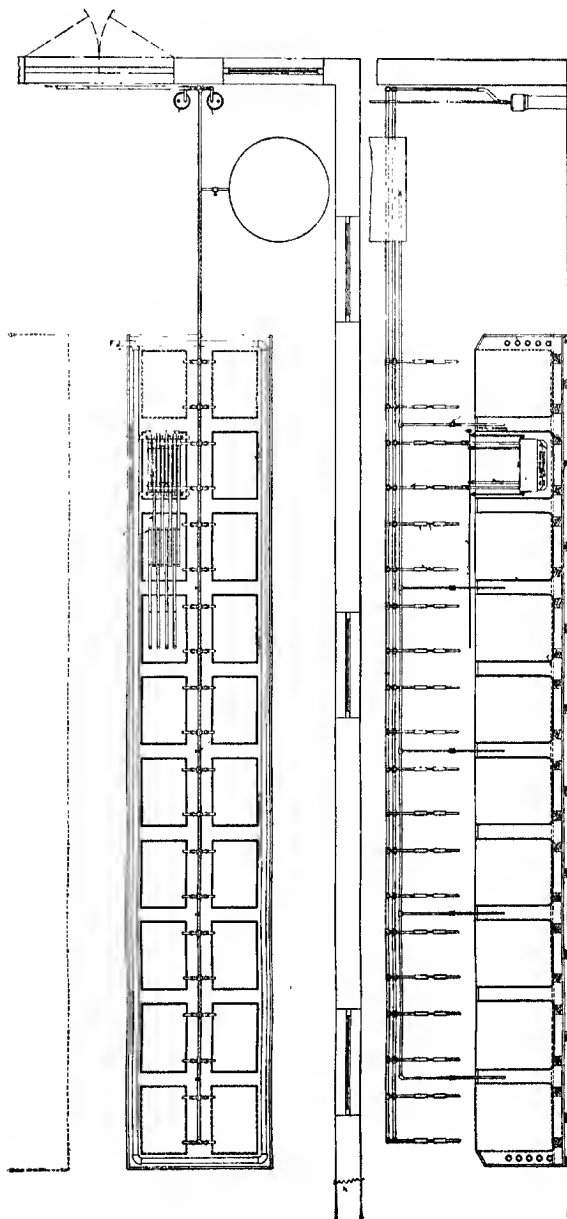


FIG. 124. Oxygen-hydrogen plant. Schuckert type.

gen and oxygen are given by **Van Scoyoc** (U. S. Patent 813,844, Feb. 27, 1906), in which the operation is rendered continuous by the use of automatic float-valves. The level of the acidulated water in the electrolyzer is maintained constant by means of a float-valve in the supply pipe. The two electrodes are placed in two compartments which are open at the bottom. Each compartment is divided into a lower and an upper chamber, connection between the two being made by automatic float-valves. When the pressure of the gases generated in the lower chambers becomes great enough to lower the level of the water, the valve is opened and the gases pass into the other chamber and then into gas bags.

**Aigner**\* charges an alkaline electrolyte into an iron vessel *G*, Fig. 125, in which an iron drum *T* rotates, the outer surface of the latter being amalgamated.

The upper part of *G* is divided into two compartments *R* and *R<sub>1</sub>* by the partition *S*, which extends downwards nearly to the drum *T*. The oxygen and hydrogen are led off through separate outlets in the cover *D*. The electrolyte is introduced and withdrawn through the opening *L*. At the anode *A* hydroxyl ions are depolarized, with formation of water and gaseous oxygen, the latter escaping into the compartment *R*, while an equivalent quantity of sodium ions is depolarized and combines chemically with amalgam on the surface of the drum adjacent to the anode. When this portion of the drum comes below the cathode *K* hydroxyl ions are depolarized with formation of sodium hydroxide, the sodium being redissolved from amalgam, while sodium ions are depolarized with formation of sodium hydroxide and gaseous hydrogen.

The electrodes of the **Cowper-Coles** generator† consist of metallic sheets provided with tongues, which project downwards at an angle of about 45 degrees with the faces of the sheets. These electrodes are placed in separate collecting boxes or chambers, the liberated gases being guided into the latter by the inclined tongues of metal which project within openings in the sides of the chambers. A battery of generators may be enclosed in a water jacket and provided with means for keeping the solution in each cell at a common level.

**Dansette** (French Patent 391,793, Sept. 6, 1907) has devised an arrangement for feeding water vapor into the zone of an electric arc produced in a gas-tight electric furnace, by passing water through the lower, vertical, carbon tube, which constitutes one of the electrodes. The furnace communicates by means of a valve with a reservoir, into which the hydrogen and oxygen produced by dissociation pass. The oxygen may either be absorbed by a suitable reagent, or the two gases separated by diffusion through a porous earthenware vessel.

\* German Patent 198,626, Nov. 13, 1906.

† British Patent 14,285 Dec. 20, 1907.

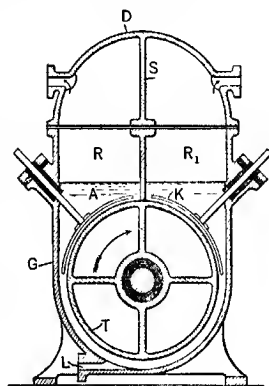


FIG. 125.

An electrolyzer for the production of pure hydrogen and oxygen which is suggestive of the Schmidt type has been designed by **Eycken, Leroy and Moritz**.<sup>\*</sup> The electrode plates are built up with separating diaphragms of asbestos, in the form of a filter-press. Openings in the top of each plate form two channels for the escape of the gases. The gases are kept at a pressure above that of the atmosphere, rendering the danger of accidental mixing remote. The electrodes and diaphragms are kept clean by making the first electrode hollow, and in the form of a large reservoir, in which the sediment accumulates and from which it may be removed from time to time. This reservoir is divided into two parts, into which the gases pass, through the electrolyte, the pressure being maintained constant, and the delivery of the gases regulated by two floats and balanced valves.

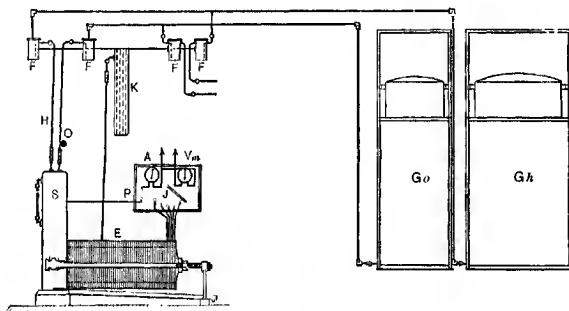


FIG. 126.

Siegfried Barth of Dusseldorf builds "oxhydrogenerators" constructed in accordance with the foregoing system. The parts of the generator are very heavy so that durability is insured. The electrode plates are insulated by extra heavy, almost indestructible, diaphragms. A very powerful circulation of the electrolyte over the surface of the electrode is obtained, resulting in an efficient removal of the gas particles which otherwise would cling to the electrodes for a considerably longer period. Great pains have been taken to guard against mixing of the gases so as to procure pure products. Caustic soda or potash in distilled water is used as the electrolyte. When used uninterruptedly, the cell becomes warm and its output is improved, and for intermittent operation a steam-heating arrangement is attached to the generator so that it may be heated quickly and brought to full capacity without loss of time. The ordinary type of this generator is made to deliver both hydrogen and oxygen under a pressure of about 50 to 80 cubic meters water column, but special forms are furnished which operate under a pressure of about 4 kilos (8 to 9 pounds). A generator having an output of 6.6 cubic meters of hydrogen and 3.3 cubic meters of oxygen per hour, requiring 160 amperes at 250 volts is 4.4 meters

<sup>\*</sup> French Patent 397,319, Dec. 9, 1908.

long, 0.72 meter wide, and 2.05 meters in height, and weights 6600 kilos; the cost being \$2175. (Fig. 126.)\*

Another apparatus of the filter-press type † is designed especially to produce the gases at relatively high pressure without the purity of the product being affected. Fig. 127 shows a form of electrode plate and Fig. 128 a view of one end of the generator, showing a collecting tower with regulator float and a series of plate electrodes.‡ §

The electrolytic cell of Tommasini as shown in Fig. 129 contains vertical anodes 6 and cathodes in the form of inverted U-shaped receptacles 5. The outside of these receptacles 5 is covered with an insulating apron 7 which extends to a point above the liquid line, and to a point below the lower edge of the cathode 5 proper, so that an overhanging apron 8 is provided. The gases evolved at the plates 6 and accumulated in the top of the inverted receptacles 5 are conducted off separately, the hydrogen passing through the pipe 12 into the safety device 14. The height of water is less in the safety device 14 than in the receptacles 5, so that when the pressure of the hydrogen gas becomes so great as to tend to press the fluid out of the chambers 5 (which would result in the mixing of the hydrogen with oxygen) the pressure of the hydrogen gas will first press the water out of the receptacle 19 and pass out of slots 20, so as to relieve the pressure in the receptacles 5. The aprons 8 at the bottom of the compartments 5 also prevent mixing of the two gases. ||

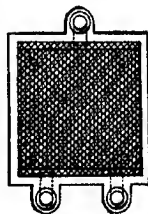


FIG. 127.

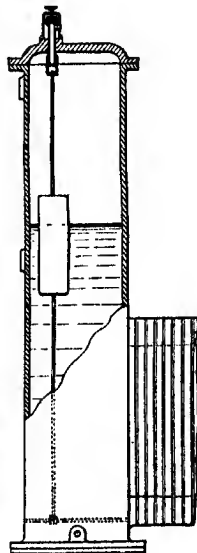


FIG. 128.

\* A multiple-cell electrolytic generator has been patented by Levin, U. S. Patent 1,094,728, April 28, 1914, assigned to the International Oxygen Co.

† Moritz, U. S. Patent 981,102, Jan. 10, 1911.

‡ In the generator of L'Oxydrique Francaise (French Patent 459,967, Sept. 21, 1912, and addition, June 25, 1913), the diaphragm of each element is composed of asbestos fabric, which is nipped between two wooden frames. The latter are bored so as to provide conduits for the evolved gases and the electrolyte. The electrodes are composed of light sheet iron, grooved or corrugated, so as to possess as much active surface as possible. The electrodes may be nickelled on their anode sides. The apparatus comprises a series of such elements.

§ See also U. S. Patent *Reissue* 13,643, Nov. 11, 1913.

|| U. S. Patent 1,035,060, Aug. 6, 1912.

Buffa (Electrician (1900), 46) states that one of the chief difficulties met with in the electrolysis of water on the large scale is the mixing of the oxygen and hydrogen given off at the two electrodes. If, in order to avoid this mixing, a diaphragm be introduced, the resistance of the cell increases to such an extent that the efficiency of the apparatus is seriously reduced. A better method is to use metallic septa; these separate the two gases perfectly, and act as intermediate electrodes. Since the reduction of voltage, both from the anode to one side of the septum and from the other side of the septum to the cathode, is insufficient to cause decomposition

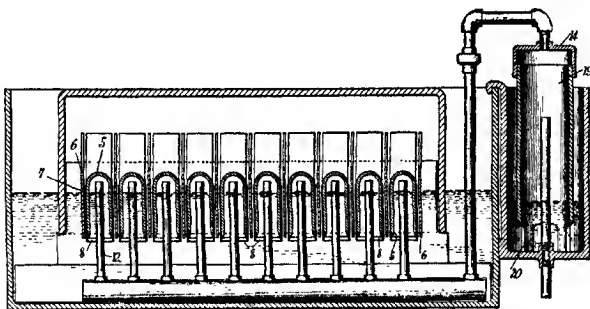


FIG. 129.

of the water, liberation of the products of electrolysis does not occur at either surface of the metallic septum, but is confined to the electrodes proper. In practice, iron electrodes in a 11 per cent solution of caustic soda have been found to be most convenient and economical. The electrolyte is covered with a film of mineral oil, in order to prevent absorption of carbon dioxide from the air. It has been observed that the same protective action is afforded by a film of water vapor, which obtains when the temperature of the electrode is fairly high; when, however, the temperature drops to 10° C. or under, absorption of carbon dioxide takes place rapidly.

With the object of completely preventing admixture of the two gases and at the same time keeping the electrical resistance low, **Vareille** arranges the electrodes as shown in Fig. 130. Vertical rows of V-shaped troughs are provided with suitable insulation and serve to separate the positive and negative electrodes which are placed on opposite sides. The extremities 20 of these troughs are lower than the ends of the electrodes 13, so that the bubbles of gas coming from the latter cannot mix. The electrodes are both insulated from the container.\*

In a modification, the troughs, described above, for the separation of the electrodes are replaced by vertical series of elements each of triangular section, and either solid or hollow. Each electrode consists of a sheet, with U-shaped pieces bound on each side with rivets. The gases are collected in bells, either stamped out of sheet metal or consisting of sheets cut out and folded, and united at the angles by autogenous soldering.†

\* French Patent 355,652, June 27, 1905, and U. S. Patent 823,650, June 19, 1906.

† First addition, Oct. 28, 1908, to French Patent 355,652.



Water is made more conductive, according to McCarty (U. S. Patent 736,868, Aug. 18, 1903), by the addition of tartrate of potassium, tartrate of sodium, or any of the citrates or other equivalents, and sulfuric acid. The apparatus (U. S. Patent 721,068, Feb. 17, 1903) consists of two tanks, connected by a pipe at about half their height. Each tank consists of an electrode, so located that the upper ends are about in a line with the axis of the connecting pipe, through which the current passes from one tank to the other. Each of the two tanks has an outlet at the top through which the gases generated may be led to suitable holders.

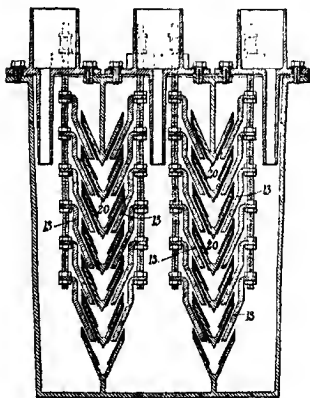


FIG. 130.

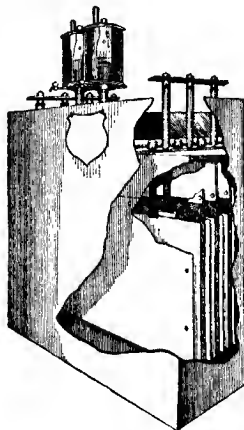


FIG. 131.

Another apparatus (McCarty, U. S. Patent 816,355, March 27, 1906) consists of two receptacles, each containing one electrode and connected by a conduit near the bottom. Each electrode is a plate of platinum coiled upon itself a number of times and has a projecting terminal portion directly opposite the end of the conduit. In still another type (McCarty, 814,155, March 6; see also 813,105, Feb. 20, 1906) the electrolytic cell is divided into two compartments by means of a solid diaphragm, which is perforated, short glass tubes being inserted in each perforation.

The **Burdett system** \* of electrolytic apparatus consists of a varying number of generators or units, connected electrically in series. The unit, Fig. 131, comprises a container enclosing the electrodes and electrolyte, but the walls of the container do not function as electrodes. It is usually mounted on concrete foundations and is insulated both from the ground and from the generator proper. The electrodes are arranged on the multiple system, there being a number of both positive and negative electrodes in each unit. The electrodes are separated from each other by a partition of specially-prepared asbestos cloth which under the conditions of operation is permeable to the solution but not to gas.

\* U. S. Patent to Burdett, 1,086,804, Feb. 10, 1914.

A bell or box casting, open at the bottom, is used for housing the electrodes and the asbestos diaphragm is stretched across the box casting from one side to the other, forming a number of compartments. In each of the compartments an electrode is placed running parallel to the asbestos curtain or diaphragm. The electrical connections are so arranged that commencing with and including the first electrode, every other electrode is a cathode, the alternate electrodes being anodes. At the top of the container the electrode terminals are joined by means of copper bus bars, thus bringing all the anodes to a common anode terminal and all of the cathodes to a similar connection.

The gas generated at the electrodes rises and is collected in the separate gas-tight compartments. These compartments are joined by two cored gas passages in the bell casting and the gases pass through these passages into and through glass indicators and purgers to the gas mains. Inserted in each of the service mains is a gas meter, a flash-back, and a water purger which removes the water held in suspension in the gas and at the same time acts as a pressure regulator for the generators. Purifiers are usually inserted in each line to cleanse the gas. The hydrogen and oxygen are led to their respective gasometers and from there are compressed into storage tanks for use. By means of controls the compression may be taken care of automatically.\*

The automatic control feature of the Burdett apparatus is useful. By means of electrical regulating devices the entire electrolytic equipment is under automatic control. It also serves as a safety device, preventing over-generation of gas or undue pressure on any parts of the apparatus. The compressor, when the collecting gasometer reaches a predetermined height, will automatically start, and will stop when the gasometer falls to a predetermined level. Electric control is provided which will stop the motor of the compressor when the storage tank pressure reaches a certain point, starting the motor when the pressure falls again, and another control is provided which will stop the generation of gas when both gasometer and storage tank are charged to their full capacity.

Fig. 132 shows a battery of Burdett generators and Fig. 133 illustrates a complete equipment embracing motor-generator, gasometers, storage tanks and automatic control devices.

Each generator operating under a current of 400 amperes will produce in excess of 6 cubic feet of hydrogen and one-half this amount of oxygen per hour, or in round numbers, 150 cubic feet of hydrogen and 75 cubic feet of oxygen per 24-hour day

\* The author is indebted to Mr. Paul Pleiss for a description of the Burdett generator, also for some data on the Garuti and Schuckert cells.

with the gas measured at 20° C. and 760 mm. It is desirable to operate the plant as continuously as possible and a run of 23 or 24 hours per day is recommended.

Each cell operating under normal conditions will require, with a solution temperature of 80° F. about 2 volts for the passage of 400 amperes. Thus each cell requires about 800 watts (0.8 kilowatt-hour) per hour to produce about 6 cubic feet of

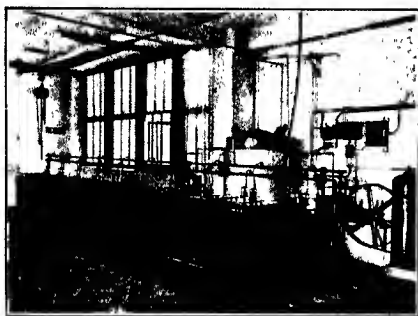


FIG. 132.

hydrogen per hour. The efficiency of the generator is therefore high. If the cell generator be artificially heated the consumption of electricity may be decreased by about 10 per cent with a corresponding increase in the efficiency of the unit. The hydrogen will average in purity 99 per cent or higher.

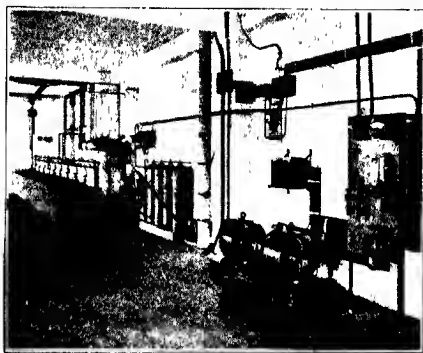


FIG. 133.

Electrolytic apparatus designed by **Hazard-Flamand** \* is shown in Fig. 134. Between the inner and outer electrodes a porous diaphragm is inserted and a fluid seal is disposed about both sides of the top of the

\* U. S. Patent 1,003,456, Sept. 19, 1911, assigned to the International Oxygen Co.

diaphragm and is composed of an outer seal and an inner seal, consisting of two concentric troughs one within the other. The electrolyte is fed into the inner trough, passes to the outer trough and is delivered from the latter on both sides of the diaphragm.\*

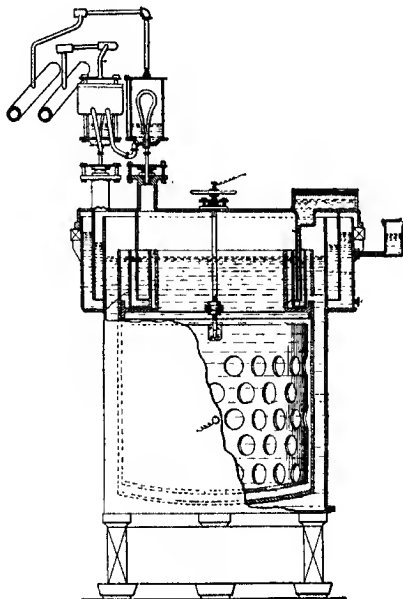


FIG. 134.

The **I. O. C. System** (International Oxygen Co.) is a well-standardized method of generating hydrogen and oxygen. The electrolytic cell used is very simple, an outside view being given in Fig. 135 and a diagram in Fig. 136. The iron tank or container serves as the cathode, being connected to the negative pole of the electric supply circuit. From the cover of this tank is suspended a perforated tank which serves as the anode, being connected to the positive pole of the supply circuit. It is made of a specially selected low-carbon steel, to prevent the formation of spongy rust. By means of an asbestos sack, suspended from the cover between anode and cathode, two separate compartments are formed. At the top these compartments are sealed by a hydraulic joint. Through an opening in the cover a solution of caustic alkali in distilled water is poured into the hydraulic

\* See also U. S. Patent 646,281, March 27, 1900, to Hazard-Flamand.

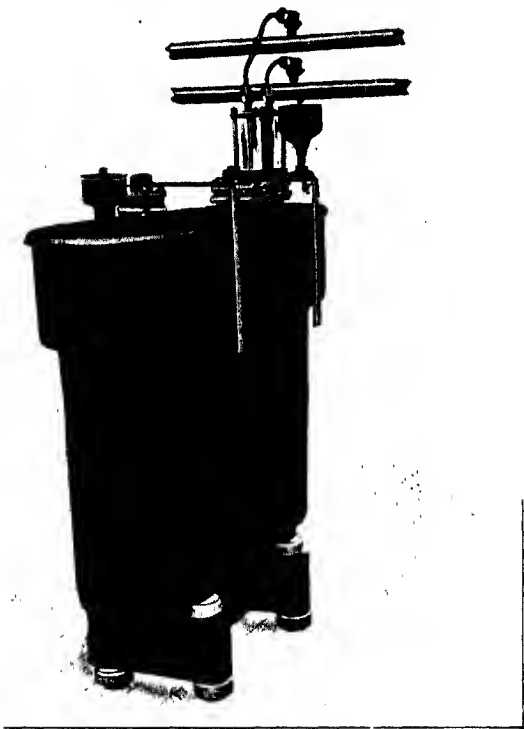


FIG. 135.

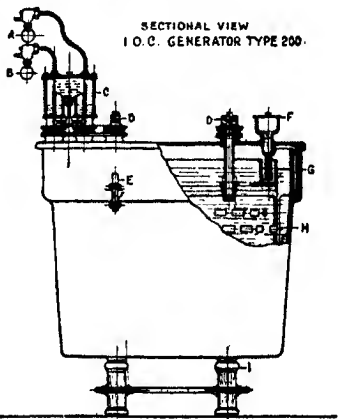


FIG. 136

joint and distributed in the two compartments. The whole cell is placed on insulating supports of porcelain.

The oxygen and hydrogen gases evolved do not pass directly from their compartments to the off-take pipes, but first bubble through water contained in the two "lanterns" on top of the cell. They enable the operator to see at a glance how the cell is working. The purity of the gases produced is very high. A sample of hydrogen produced



FIG. 137. Battery of I. O. C. generators.

by this electrolyzer, analyzed by the Conservatoire National des Arts et Metier in Paris, showed 99.70 per cent hydrogen, the fraction of the impurities being so small that they were not examined.

All that is required for the operation of the cell is the daily addition of somewhat over a gallon of distilled water to make up for the quantity decomposed into hydrogen and oxygen. The daily output is approximately 72 cubic feet of oxygen and 144 cubic feet of hydrogen. As to the electrical energy requirements a joint test \* made in November, 1910, by the Laboratoire Centrale de l'Electricite and the Conservatoire National des Arts et Metier with two unit cells of this type of electrolytic cell showed that the production of 1 cubic foot of oxy-

\* Met. and Chem. Eng. (1911), 471.

gen and 2 cubic feet of hydrogen requires 0.2797 kilowatt-hour. Reversely 1 kilowatt-hour produces 3.54 cubic feet of oxygen and 7 cubic feet of hydrogen. Each unit cell requires a little above 2 volts and from 300 to 400 amperes. A current of 350 amperes produces about 65 cubic feet of oxygen and 130 cubic feet of hydrogen per day.

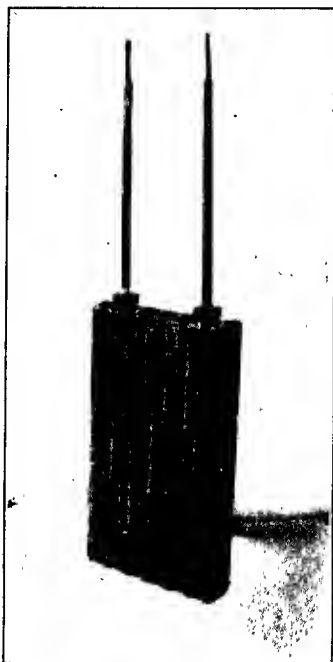


FIG. 138.

The following table gives the results of a test recently made by the Electrical Testing Laboratories of New York for the International Oxygen Co.

Cell No.	Average amperes	Average volts	Average watts	Maximum temp.	Purity of oxygen	Cubic feet per hour		Cubic feet per kilowatt-hour	
						Oxygen	Hydrogen	Oxygen	Hydrogen
8.....	405.1	2.388	967	31.8° C.	97.73%	3.247	6.184	3.358	6.395
14.....	405.0	2.562	1038	30.0° C.	98.67%	3.239	.....	3.120	.....
66.....	368.8	2.826	1042	32.0° C.	98.46%	2.886	5.788	2.770	5.555
70.....	392.0	2.660	1043	26.5° C.	98.50%	3.082	6.254	2.955	5.900
Average.....	392.7	2.609	1022	30.1° C.	98.34%	3.114	6.075	3.051	5.950

The four cells tested were selected as being representative of the entire battery after taking a set of preliminary electrical measurements on each of the cells.

All of the data given herewith are from readings as actually observed and corrected for instrument errors. Gas volumes are corrected for moisture and calculated to 20° C. and 760 mm.

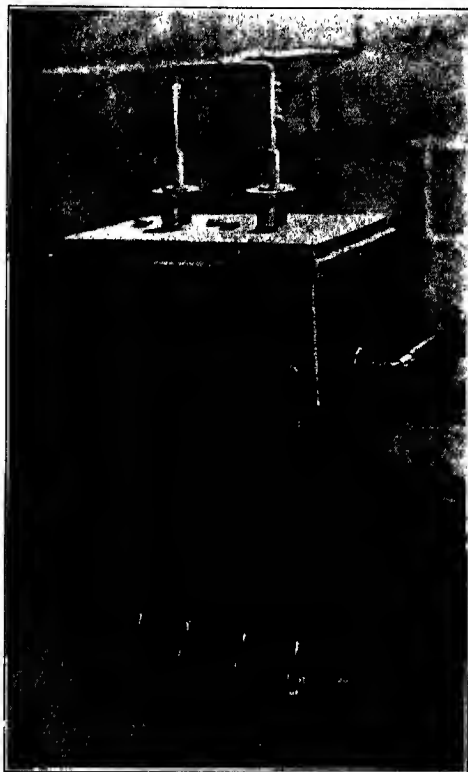


FIG. 139.

The main item of operating expense is the cost for the electric current. In New York City the wholesale rates are higher than in many other large cities and vary from 5 to 3 cents per kilowatt-hour, according to the size of the plant; since 1 kilowatt-hour produces about 3 cubic feet of oxygen and 6 cubic feet of hydrogen, the electric power cost for producing 1000 cubic feet of oxygen and at the same time 2000 cubic feet of hydrogen would be between \$16.70 and \$10.00. However, in large manufacturing plants which have their own power houses the cost of energy is much less; thus it is known that at the South Chicago works of the U. S. Steel Corporation the electrical energy supplied to the electric furnaces is charged at the rate of half



a cent per kilowatt-hour. At this rate the electric power cost for producing 1000 cubic feet of oxygen and 2000 cubic feet of hydrogen would be \$1.67.

Besides the electric power cost there is the cost for distilled water and for attendance. The latter is a small item, and the cost for the distilled water which must be added to the cells to make up for the water electrolyzed may be calculated from the fact that a little over 6 gallons of distilled water are required to produce 1000 cubic feet of hydrogen.

One of the objections advanced against the electrolytic system is the relatively large floor space which it occupies, and to obtain an apparatus of a durable yet compact character the author has designed a generator having T-shaped ribs on both anode and cathode, affording a large generating surface without excessive bulk. Fig. 138 shows a form of anode and Fig. 139 the assembled generator.\*

A description of the Bettendorf, Iowa, Plant is given † as a typical electrolytic oxyhydrogen plant. Fifty generating cells are connected in series across a 110-volt direct current line, each cell requiring 400 amperes at 2.2 volts and producing about 3.5 cu. ft. of oxygen and 7 cu. ft. of hydrogen per kilowatt hour. The output per twenty-four hour day is 4000 cu. ft. of oxygen and 8000 cu. ft. of hydrogen. The oxygen is 99.5 per cent and the hydrogen 99.9 per cent pure. The gases are stored in large tanks and for shipment they are compressed at 1800 lb. per square inch into 100 or 200 cu. ft. steel cylinders. The current for the cells is obtained by means of a motor generator set: 440-volt 3-phase, 60-cycle induction motor connected to a 50-kilowatt shunt wound, commutating pole generator. A 20 horsepower boiler furnishes distilled water for the cells.

An electrolytic oxygen and hydrogen plant put into operation ‡ by the National Ox-Hydric Co., of Chicago, at the works of the Fore River Shipbuilding Corporation, Quincy, Mass., is simple to operate, requiring the attention of only one man to a shift, the plant being run continuously by three men in three eight-hour shifts. The plant consists of a 75-horse-power Bessemer crude-oil engine, belt-connected to a 45-kilowatt direct-current generator; one of the National Ox-Hydric Co.'s electrolyzers, producing 3500 cu. ft. of oxygen per twenty-four hours and twice that amount of hydrogen; suitable gasometers, compressors, motors, and switchboards for control. The oxygen and hydrogen, after being produced from the electrolyzer, pass into steel gasometers of 2000 cu. ft. capacity each. The National electrolyzer is of the improved filter-press type and consists of a number of decomposition chambers connected in series. These chambers are formed by clamping together a series of cast-iron electrodes so recessed and grooved that each plate forms, with its neighbor, a chamber which holds the electrolyte, and in which the generation of the gases takes place. The electrodes are insulated one from the other by means of rubber-bound asbestos diaphragms. The electrodes and diaphragms are arranged alternately and are supported by the insulated frame of the filter press. The required number of electrodes and diaphragms with the corresponding end plates are then pressed tightly together by means of a heavy screw standard, thus making the whole equipment form a hermetically sealed tank, the diaphragms serving both as an insulation and gasket, and serve to form the sides of the cells, preventing mixture of

\* U. S. Patent 1,087,937, Feb. 24, 1914.

† Elec. Rev. West. Elec., 66, 1170, 1915; Chem. Abs., 1915, 2189.

‡ Met. Chem. Eng., 1916, 288.

the two gases generated. The fact that the electrodes are thus separated by the diaphragms causes one side of the plate to act as the anode of one chamber and the other side as the cathode of the adjacent chamber. The electrodes are composed of a special alloy, and are heavily coated with nickel, which prevents the formation of deposits or the oxidation of the electrodes themselves. The electrolyzers are designed for any standard direct current circuit, or with the use of a motor-generator set, for any of the standard alternating current circuits, thus doing away with the inefficient low voltage, high amperage equipment necessary with the individual-cell type installation. These electrolyzers are stated to occupy about one-fifth the floor space required by the individual cell type. The electrodes themselves are made with corrugated surfaces, increasing the active electrode surface and forming a large number of very small vertical channels through which the gases rise freely to the upper part of the plates. At the top of each electrode and hermetically sealed together are chambers in which the gases are separated from the electrolyte. From these chambers the gases pass off into ducts extending through each plate, these ducts forming continuous conduits, owing to the manner in which the plates are assembled. The electrolyte is a 21 per cent solution of pure caustic potash in distilled water. After the electrolyzers are once filled with this solution, distilled water is added from time to time to take the place of the water decomposed; the potash lasts many months. The distilled water is fed to the electrolyzer by an automatic device which maintains a constant level of the electrolyte throughout the machine. Under normal load conditions, the voltage required per cell is two volts or less. Therefore, to operate on a 110-volt circuit an electrolyzer containing 55 cells is necessary; and on the same basis, 110 cells are necessary for a 220-volt circuit. The positive pole of the direct-current dynamo is connected with the first electrode in the series, and the negative pole is connected to the last electrode of the series. The apparatus is provided with one collector for hydrogen and one for oxygen, whereas, the individual-cell type system must have a separate draw-off, or collector, for each cell in use. Assuming continuous operation and normal load conditions as specified, the electrolyzers yield 4 cu. ft. of oxygen and 8 cu. ft. of hydrogen at atmospheric pressure per kilowatt hour of power consumed when the plant is operated at a temperature of 68° F.

The International Oxygen Company has developed a new style oxygen and hydrogen generator of the filter press type under the name of the I.O.C. bipolar generator.\* See Figs. 139*a*, 139*b* and 139*c*.

The unit type of generator produces 3.2 cu. ft. of oxygen and 6.4 cu. ft. of hydrogen per clock hour and 4 cu. ft. of oxygen and 8 cu. ft. of hydrogen per kilowatt hour.

The I.O.C. Bipolar Generator consists of a series of metallic plates (electrodes) clamped together in a heavy frame, electrically insulated from one another and separated by diaphragms of porous fabric. Each pair of these electrodes forms a closed cell, divided by the diaphragm. These cells are filled with an alkaline electrolyte (caustic potash or soda). An electric current admitted at one end plate passes on through the plates and the solution to the other end plate. In its passage, it decomposes the water in the solution into the two gases—oxygen and hydrogen which are released on opposite sides of each plate and emerge upward into the gas oftakes.

\* Levin; U. S. Patent No. 1,094,728; French Patent No. 467,945, Jan. 31, 1914; British Patent No. 3,654, Feb. 12, 1914; Met. Chem. Eng., 1916, 108; U. S. Patent No. 1,199,472.

The mingling of the oxygen and hydrogen in each cell or compartment is prevented by the diaphragm which, as the gases are released and withdrawn, the solution is automatically replenished from a supply tank. The operation is continuous so long as current and electrolyte are supplied. In the smaller type of generator, the electrodes are carried on two steel rods supported on two heavy end pieces or pedestals of cast iron. In the larger generator, the side rods are replaced by steel bars. The construction is one of extreme rigidity, absolutely proof against any distortion and consequent disarrangement of electrodes, with resultant leakage. The electrodes are clamped together by a heavy screw working in the rear support. A ball thrust bearing is interposed between the end of the clamping screw and the rear end plate, contributing to the tightness of the generator by doing away with the tendency of the electrodes to "ride up" from the side bars under screw pressure. The elec-

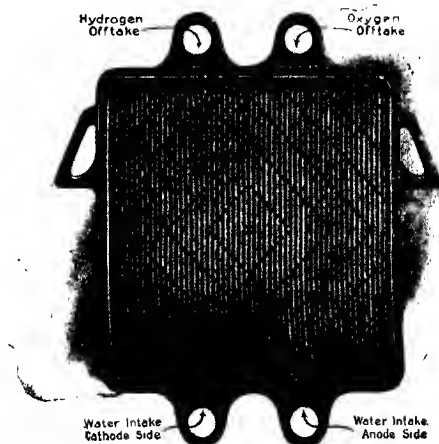


FIG. 139a.

trodes are of a special design,\* the anode side being heavily nickled, while the cathode side is of commercially pure iron. The surfaces of the electrodes carry vertical corrugations which are interrupted by a large number of depressions to facilitate the flow of electrolyte into the cell and the release of the gases from it. At top and bottom of each electrode are two openings communicating by a cored channel with opposite sides of the plate. Those at the bottom are for the water intake and those at the top are for the gas offtake. Each half of each cell (separated by the diaphragm) has its own independent water intake and gas outlet, so that there can be no possibility of the two gases mingling through these channels. Any gas leakage which may occur between the electrodes escapes to the open air and not into the adjacent cell or into the gas offtakes. The diaphragms are of especially prepared asbestos fabric. All around the edge of this fabric is moulded a packing rim of pure rubber which rests in a recessed groove on the face of the electrode.

In a generator of this kind, an essential of power economy is that all the current

\* U. S. Patent to Levin, No. 1,153,168.

supplied the machine shall pass through the electrolyte and none of it be by-passed through the metal of the machine or through the water inlets and gas outlets. The electrodes are insulated from the side bars of the frames by porcelain insulators. The electrodes are insulated from one another by the pure rubber packing rim surrounding the diaphragm, and by nipples of pure rubber inserted in the water intake and gas offtake shoulders of the electrodes. These nipples, when the apparatus is closed, meet one another and not only insulate the electrode shoulders but

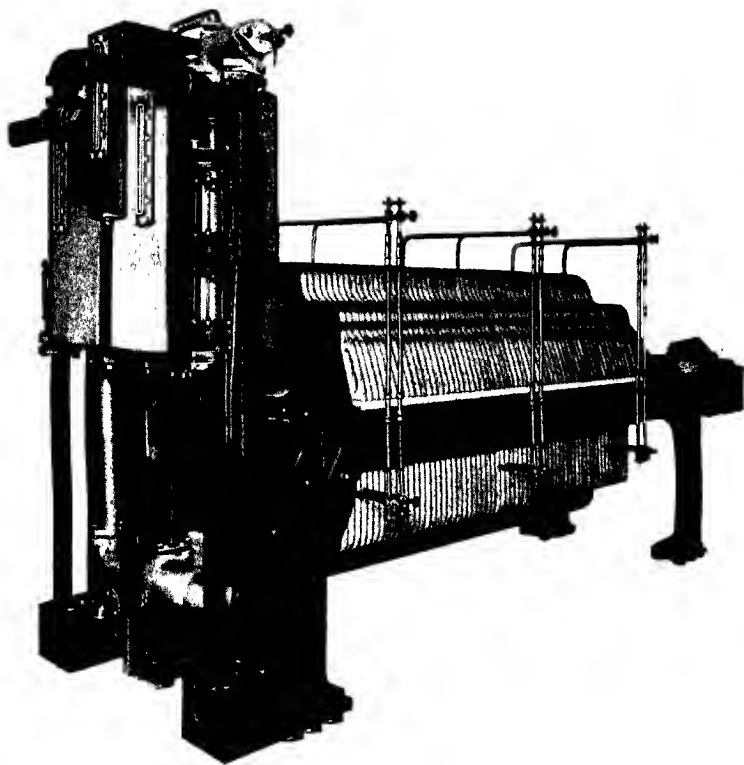


FIG. 139b.

also provide an insulating tube in the interior of the water intakes and gas oftakes. The gases rising from the electrodes and entering the gas oftakes, carry with them a small percentage of the electrolyte which, if allowed to enter the external piping system, would "ground" the apparatus and permit the escape of current. To guard against this contingency, there is provided in the gas oftake system insulating pipe sections, each consisting of two sections of heavy glass tube clamped between iron flanges and so devised as to intercept and drain off through an insu-

lating connection the moisture entrained in the gases. The gases go through these insulators substantially dry and free from electrolyte. The nickel anode and iron cathode have been found to materially facilitate the electrolysis, and to lower the over-voltage. Incidentally, these bi-metallic electrodes prevent the formation of rust and oxides which would shorten the life of the apparatus. The design of the generator is such as to retain within the apparatus most of the heat produced as a result of the resistance to the flow of electricity. This keeps the electrolyte and the electrodes at a comparatively high temperature, which adds to the efficiency of the electrolytic process. On the front of the generator are two tanks with glass water-level indicators, which carry the solution. Pipes descend from these tanks

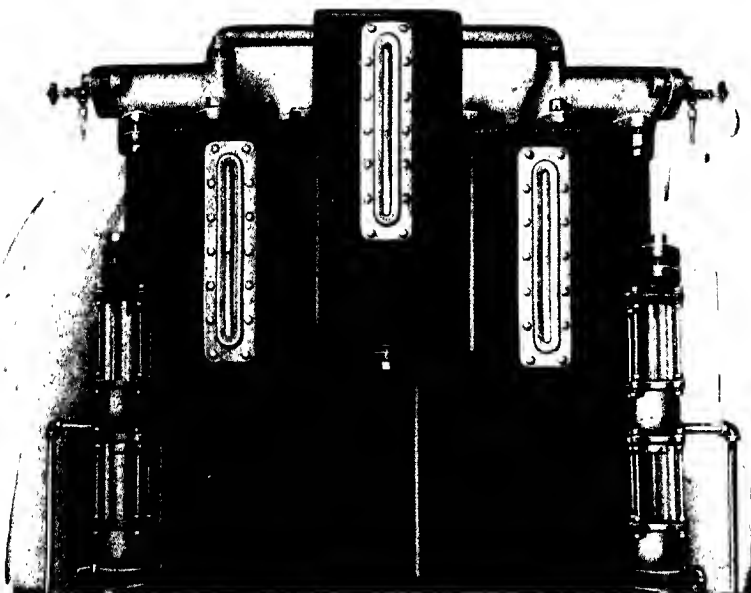


FIG. 139c.

to a water-feed manifold which branches into two pipes connecting independently to the two water intakes to the cells and also into two risers leading to two independent gas domes above. Into these domes, the oxygen and hydrogen are separately discharged as generated, the gas offtakes opening through an inverted "U" below the fluid level. The proper fluid level is automatically maintained throughout the system. The two independent water intakes to either side of each electrode prevent mingling of oxygen and hydrogen through the water supply. The two gas off-takes discharge into the two independent gas domes already referred to, the gas emerging below the fluid surface through an inverted "U." The pressure on both gases, clear back to the individual cells, is the same—this being controlled by the hydrostatic head in the domes through which the gases pass. The gases

escaping from the gas offtakes rise through the fluid in the gas domes and pass out through discharge pipes at the top of the domes—thence downward to purgers on either side. These purgers are closed boxes of cast iron filled with water to a certain level. The gases escape below the surface of the water, and pass upward through it into the supply lines to the gas holders. The function of these purgers is to catch any entrained electrolyte in the gas, to cool the gas, and to act as a water-check-valve protecting the pressure system of the generator from any undue pressure of the gasholders. A signal whistle is provided which gives notice when the level of the solution in the generator falls below the prescribed level. Glass sight-feed indicators on the solution tank and gas domes show the fluid levels and reveal the generation of the gases. Gauge glasses connecting with the electrodes at intervals along the generator show the fluid levels in the body of the apparatus.

**Shriver** \* recommends an apparatus composed of several flat plates, forming the electrodes, bound face to face to form a cell of the filter-press type, each of the plates being recessed centrally to form a cell between the faces. A diaphragm is arranged between each pair of plates to separate the gases formed on the faces of adjacent plates, the gases being led from the recessed portions to closed gas chambers above, through ducts in walls separating the chambers and recesses. The gases are conveyed from the gas chambers to horizontal ducts extending through non-recessed parts of the plates from face to face, so that the recessed portions may be completely filled with liquid to a level normally higher than the horizontal ducts, without fear of the electrolyte entering the gas ducts.†

An illustrated description of the **Oerlikon** (Schmidt) electrolyzer for the commercial production of oxygen and hydrogen is given in *Electrochem. Z.*, 22, 27–42, 1915; *Chem. Abs.*, 1915, 2190.

An electrolytic apparatus, of the filter-press type, designed by **Dohmen**,‡ is composed of a series of cells, each comprising a thin quadrilateral wrought-iron frame having a single central opening, and with two passages through the top of the frame. A detachable sheet metal electrode is secured in the opening of the frame, and the top of the latter is also provided with two gas-separating chambers one at each end. The chambers extend laterally in a downward direction to the active faces of the electrodes for conducting the gases from opposite sides to the two passages.

A hydrogen generator of the unit or sectional type placed on the market by the **International Oxygen Company** offers advantages as regards compactness, high efficiency, low cost and flexibility. Fig. 139d shows a single section or unit and Fig. 139e indicates the method of assembling the sections.

Although of the single unit type, the cell is but  $3\frac{1}{2}$  in. thick and in

\* U. S. Patent No. 1,181,549; J. S. C. I., 1916, 1023.

† See also U. S. Patent No. 1,239,530, Sept. 11, 1917; J. S. C. I., 1917, 1138.

‡ U. S. Patent No. 1,211,687, Jan. 9, 1917; J. S. C. I., 1917, 295.

consequence 100 cells can be stacked in a lengthwise space of less than 30 ft. The cells are approximately 3 ft. 6 in. wide and as installed are not in excess of 6 ft. high. They occupy less space than the filter press type. These unit cells when operating at their normal current of 600

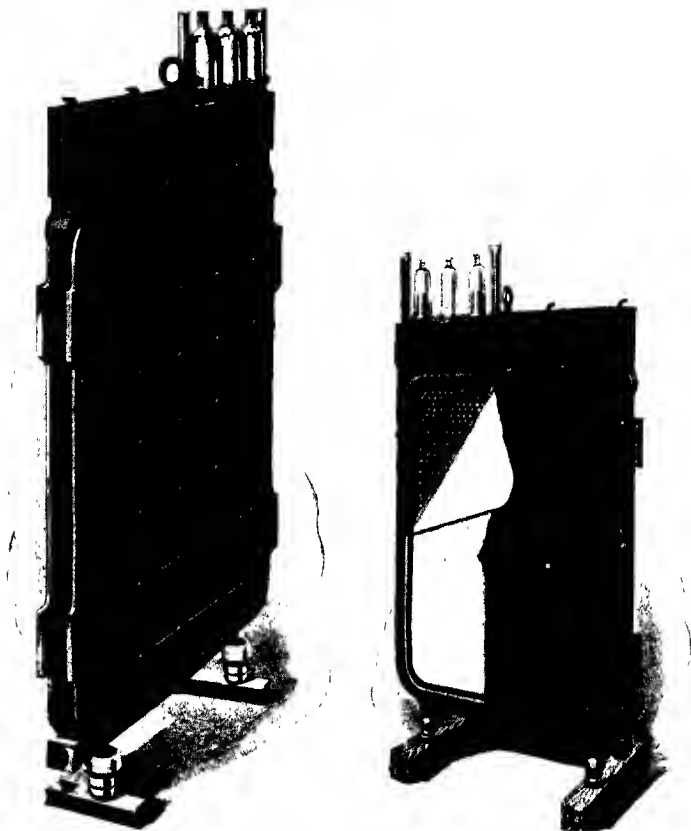


FIG. 139d.

amperes will produce 4.8 cu. ft. of oxygen and 9.6 cu. ft. of hydrogen per clock hour. They require 2.22 volts per cell which establishes a KWH. efficiency of 3.65 cu. ft. of oxygen. When operated at a current less than 600 amperes the electrical efficiency is considerably increased but the capacity is decreased and when operated in excess of 600 am-

peres there is an increase in capacity but a slight falling off in electrical efficiency; 600 amperes has, therefore, been adopted as a compromise between initial cost of installation and operating cost.

As indicating the flexibility of this equipment there is tabulated

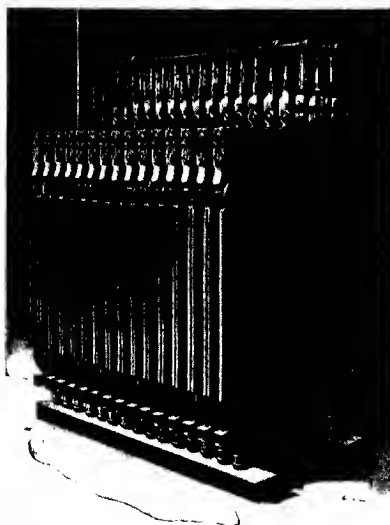


FIG. 139e.

below, the approximate performance at currents up to as high as 1000 amperes.

Current.	Volts per Cell.	Cu.ft. Oxygen per Hour.	Cu ft. Hydrogen per Hour.	Cu.ft. Oxygen per KWll.	Cu.ft. Hydrogen per KWll.
300	1.94	2.4	4.8	4.17	8.34
400	2.04	3.2	6.4	3.97	7.94
500	2.13	4.0	8.0	3.80	7.60
600	2.22	4.8	9.6	3.65	7.30
800	2.38	6.4	12.8	3.40	6.80
1000	2.54	8.0	16.0	3.16	6.32

An electrolytic hydrogen and oxygen generator with cobalt as the active anode element and iron as the cathode has been developed by Levin.\*

\* Met. Chem. Eng., 1917, 401; U. S. Patent No. 1,214,934, Feb. 6, 1917; British Patent No. 102,933 and No. 108,477, application date Oct. 27, 1916.



The generator unit consists of a rectangular thin iron plate casing of small height, long and narrow. Any number of these may be joined together to form a complete generator. The iron casing is divided into two parts by an asbestos diaphragm, suspended from an impermeable partition which reaches about one-fourth of the way down into the cell from the top. An electrode is placed in each compartment formed by the diaphragm. The partition in the upper part of the cell prevents the combination of oxygen and hydrogen after these gases have been generated and have risen separately to the top of the cell, being prevented from mixing by the diaphragm. Suitable means are provided for carrying away the gases, filling the generators with electrolyte, etc. The anode is made of iron, electroplated with a thin film of cobalt, and the cathode is of iron, preferably electrolytic. The electrodes are given a previous treatment by making them the anode in a solution of a salt of the active surface metal, and electrolyzing for a brief period. This is claimed to give greater efficiency in operation.

An electrolytic gas generator devised by Levin \* is provided with electrodes entirely independent of the container or casing. The casing is divided into three compartments, in each of which an electrode is located. The cell is of the sectional type so that a number of units may be assembled in a compact manner. The electrode compartment of the generator has a gas outlet which is sealed with water, and through which water is supplied to the compartment, from a chamber above. The water chamber is provided with a gas outlet and a water-supply conduit.†

A form of Levin generator, made by the Electrolytic Oxy-Hydrogen Laboratories, Inc. (Electrolabs) ‡ is compact and simple in construction, being built of a few standardized parts which can be rapidly and accurately assembled. The generator consists of three compartments. The oxygen is generated in the two outer compartments and the hydrogen in the center compartment. Two sheet-metal frames, to each of which is attached an asbestos diaphragm, serve as the separating mediums. The electrodes are independent of the casing. They are separated from and securely fixed within the casing by specially designed blocks of asbestos. The surfaces of both the anode and cathode are plated. The use of cobalt for such purpose is one of the features of this generator. Each compartment has an independent water feed which also serves the purpose of a blow-off device to vent the gas from each compartment under abnormal conditions. A specially designed sight-feed indicator is placed between the generator and the gas offtake pipe. Each indicator makes the generating unit to which it is attached independent of all the other generators in the group. It further serves to keep uniform the pressure of the oxygen and hydrogen inside the individual generator. It also enables one to

\* U. S. Patent No. 1,219,966, Mar. 20, 1917.

† See also U. S. Patent No. 1,247,694, Nov. 27, 1917; and 1,199,472, Sept. 26, 1916, to Levin; Chem. Abs., 1918, 253; Canadian Patent No. 175,807, Mar. 20, 1917; Chem. Abs., 1917, 3001.

‡ 15 William Street, New York City.

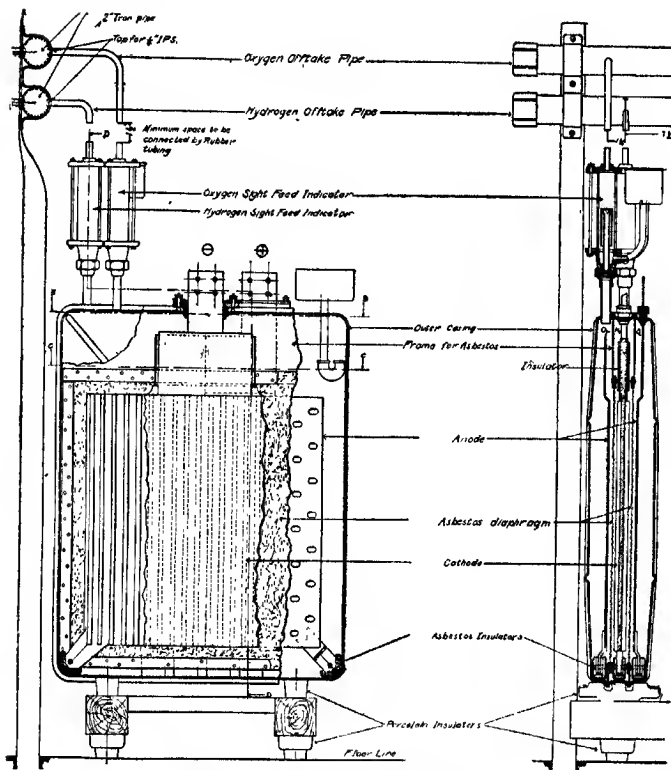
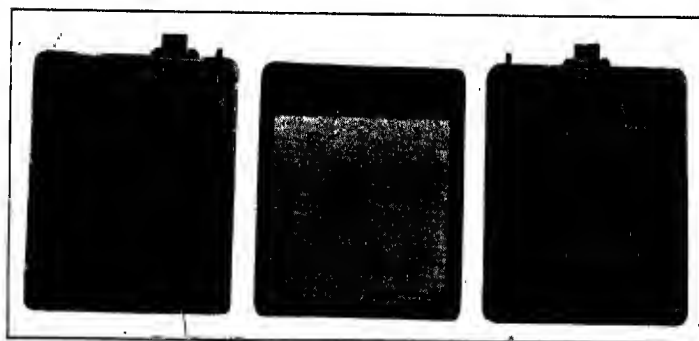


FIG. 139f.



Anode Compartment.

Asbestos Diaphragm.

Cathode Compartment.

FIG. 139g.

see at a glance whether the gases are being generated properly. The generator is delivered entirely welded and completely and rigidly assembled. The dimensions of the unit are  $30 \times 25 \times 6\frac{1}{2}$  in. The construction is shown by Figs. 139f and 139g. Fig. 139h shows the assembled unit and Fig. 139i is a group of generators.



FIG. 139h.

In a day of twenty-four hours this form of Levin generator at 200 amperes will produce 38.4 cu. ft. of oxygen and 76.8 cu. ft. of hydrogen, measured at  $20^\circ \text{C}$ . and 760 mm. pressure. A battery of 100 generators will occupy a space 31 ft. long by 4 ft. 6 in. wide and will produce.

In 1 hour

160 cu. ft. oxygen

320 cu. ft. hydrogen

In 24 hours.

3840 cu. ft. oxygen

7680 cu. ft. hydrogen

Each generator running at 200 amperes requires slightly over  $\frac{1}{10}$  kilowatt per hour.



FIG. 139i.—Electrolabs (Levin) Generators.

In a space 31 ft.  $\times$  4 ft. 6 in. and with a normal room height (10 to 12 ft.) 200 Levin generators can be installed in two tiers.

Griffin's apparatus for generating hydrogen and oxygen by electrolysis \* consists of a cell and a plate of conducting material depending into water of each cell. This plate is bent just above the cell and is attached to the adjoining cell, thus making a continuous flow of current from one cell to the next. The plate is enclosed in a sack of asbestos to separate the oxygen and hydrogen. The asbestos sack may be spaced from the plate by some insulating material to insure a complete separation of the gases. (See Fig. 139j.)

Kato states that in the electrolytic preparation of hydrogen and oxygen,† the diaphragms used in the commercial apparatus do not keep

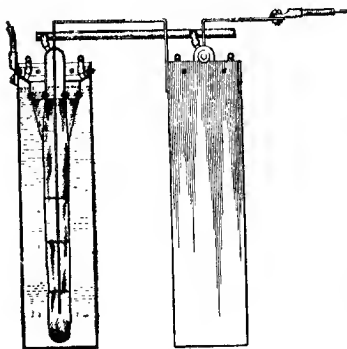


FIG. 139j.

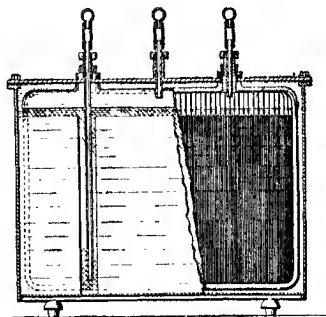


FIG. 139k.

these gases completely separate, as shown by diffusion data given. Kato finds that pure gases can be technically prepared without the use of a diaphragm. Special electrodes are employed which have an inclined active surface to which the generated gas adheres by reason of its buoyancy and accordingly does not diffuse into the solution.

Halter has devised an electrolytic cell ‡ (see Fig. 139k) for the production of oxygen and hydrogen in which a tank, acting as the cathode, is provided with a cover, from which the anode constructed of wires united in the form of a hollow body, is suspended in the electrolyte.

A separator, of porcelain or other non-conducting and oxygen-resisting material, is supported over the anode with its sides extending below the surface of the electrolyte, and the closed top is provided with an oxygen outlet. An asbestos sack is secured to and suspended from the separator, enclosing the anode below the sur-

\* U. S. Patent No. 1,117,185, Nov. 17, 1914.

† J. Chem. Ind. Japan, 18, 919, 1915; Chem. Abs., 1916, 561.

‡ U. S. Patent No. 1,172,885 and 1,172,887; J. S. C. I., 1916, 476.

face of the liquid, the separator and sack constituting a complete non-conducting enclosure for the anode. Means are provided for conducting off the hydrogen from the space beneath the cover of the separator. The tank is made in the form of a narrow upright chamber, with a partition dividing the interior of the tank into narrow vertically arranged compartments, the partition and walls of the tank forming the cathode. Each anode is formed from spaced perforated sheet-metal plates, arranged so as to have a hollow oblong form in horizontal section, with curved



FIG. 139l.



FIG. 139m.

ends and bottom, and secured at its upper edges to a horizontal conducting bar supported from the cover of the tank. A separator of non-conducting material, with attached sack enclosing the anode, is inverted over each anode and disposed lengthwise in the chamber. The partition is formed from two plates, back to back, with their end portions curved apart and around the ends of the anodes.

The Davis-Bournonville Company \* system of hydrogen and oxygen generation embraces an electrolyzer of a compact type, shown in

\* Jersey City, N. J.

Fig. 139*l*. The electrodes of this apparatus are of sheet metal, the anodes being nickeled.\* An alkaline electrolyte is used. The electrolyzers are made in two sizes, 500 and 1000 amperes, with a hydro-

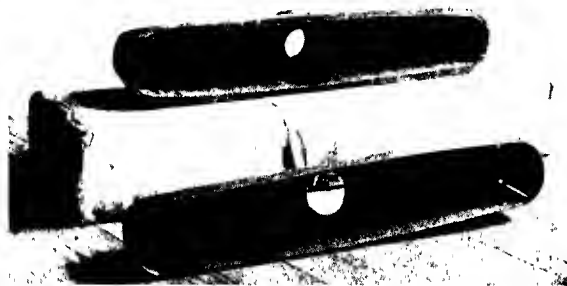


FIG. 139*n*.—Swartley Separator.

gen output of 7.92 and 15.84 cu. ft., respectively. The apparatus is assembled by the makers and is shipped ready for immediate use. Fig. 139*m* shows an anode of a 1000 ampere electrolyzer. A Swartley

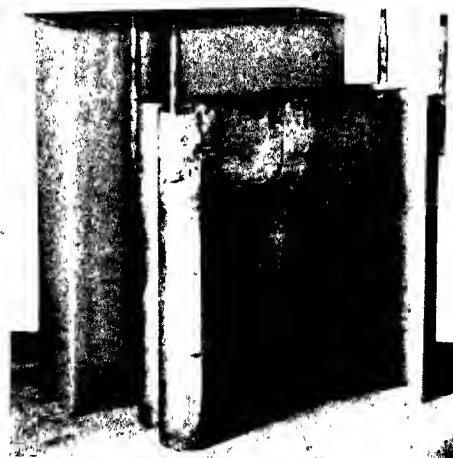


FIG. 139*o*.

hard-rubber separator † (Fig. 139*n*) is shown at the base of the anode. The separator is an inverted trough-shaped structure which is disposed

\* Swartley, U. S. Patent No. 1,263,959, April 23, 1918.

† U. S. Patent No. 1,176,105, Mar. 21, 1916.

over each anode member and extends a short distance below the surface of the electrolyte. The separator supports an asbestos sack which covers the anode member and serves to confine the oxygen. The container and partition, Fig. 139o, constitute the cathode element. Fig. 139p

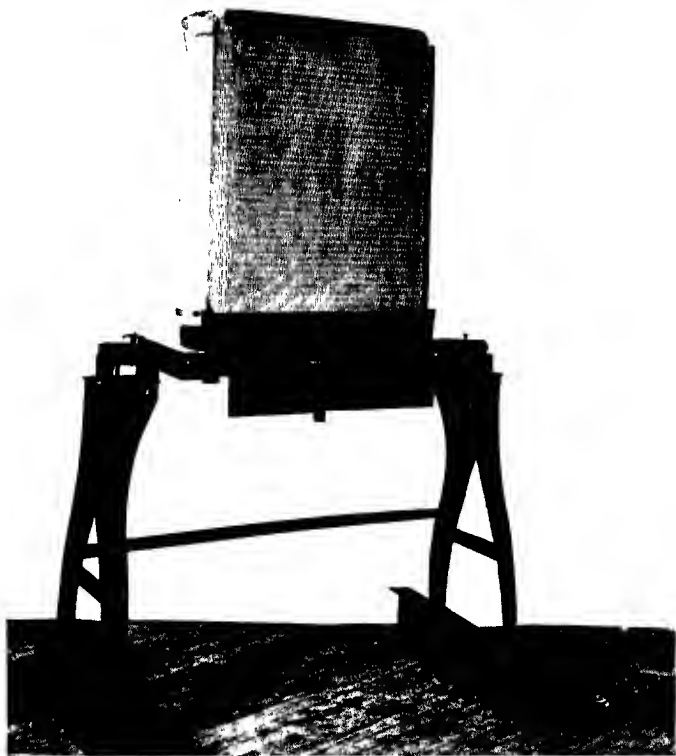


FIG. 139p.—Assembling the Anode Parts.

shows the method of assembling of anodes on the cast-iron electrolyzer cover, one anode being enclosed in an asbestos sack. Fig. 139q shows a typical arrangement of fifty of the 500 ampere electrolyzers.\*

\* This type of apparatus is made under the Bucknam Patent No. 1,172,932, Feb. 22, 1916. A description of the Davis-Bournonville equipment is found in *Oxy-Acetylene Welding* by Miller, New York, 1916, 30.

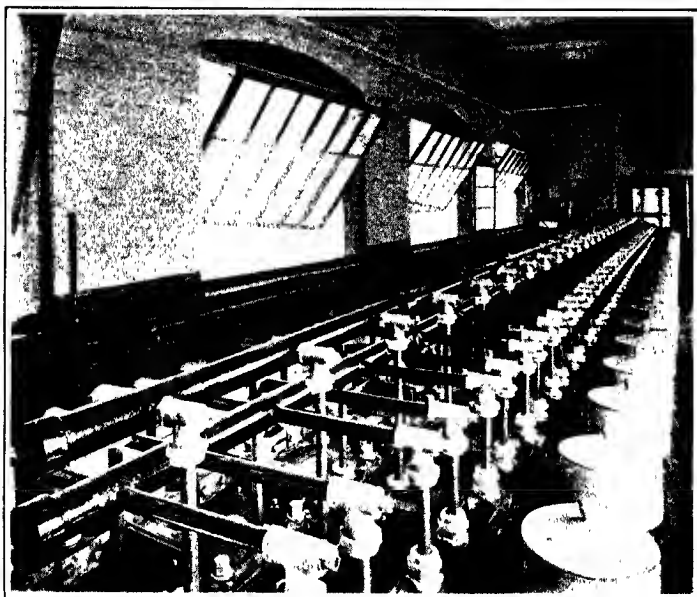


FIG. 139g.

## SYSTEM OF AUTOMATIC CONTROL

The control of the electric current employed in electrolysis of water to produce oxygen and hydrogen is of importance. Precautions must be taken against the discharge of current in a reverse direction from the electrolyzers through the generator. This condition, if allowed to develop, may result in reversal of the source of energy and consequent reverse functioning of the electrolyzers with the attendant mixing of gases. There is also to be observed the prevention of improper connection of terminals at the bank of electrolyzers during or after overhauling or for other reasons. The **Davis-Bournonville Company** has developed an electrolyzer control which is designed to prevent reversal of current direction through cutting off the source of supply automatically.

Fig. 139r shows, in a general manner, the electrical connections and methods of control. Fig. 139s shows the equipment assembled on a panel. The necessary indicating volt and ammeters *C* and *D*, respectively, are mounted on each panel of this design; also, the necessary instruments for the automatic control of the electrolyzing



circuit. The generator *A* is the source of electrical energy for the electrolyzers and its field regulator *B* is also mounted upon this panel.\*

The electrolyzer current proper, *H*, is controlled solely through the magnetic contactor *F*, the magnetic coil of which is wound for operation across the independent supply mains *G*. This independent supply main can be either alternating

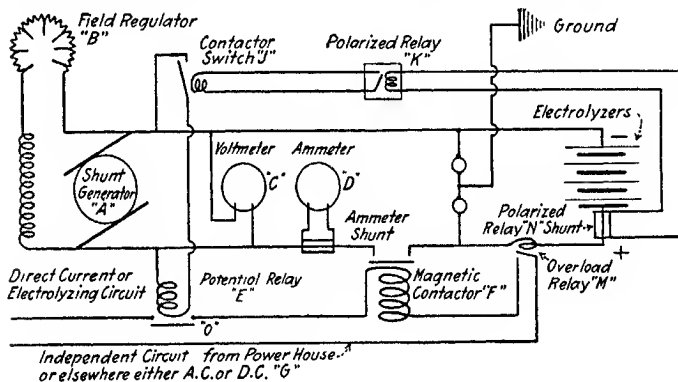


FIG. 139r.

or direct current of any voltage. This independent circuit *G* is controlled at three separate and distinct points, as follows:

- 1st—Potential Relay *E*,
- 2d—Contactor Pilot Switch, hand reset, *J*,
- 3d—Overload Relay, hand reset *M*.

The potential relay *E* is set to lift at a predetermined operating or charging voltage, thereby completing the electric circuit, which will throw into play the magnetic contactor *F*. This means that with the contactor pilot switch *J*, held closed and the overload relay closed, not until the generator will have reached the predetermined charging voltage will the potential relay close the independent circuit from the power lines. It will be noted that it is impossible to pass electrical energy through the electrolyzers until the generator attains the charging voltage.

If, for any reason, during operation the generator voltage should drop below the charging voltage, the potential relay *E* will automatically drop out, opening the magnetic contactor, thereby breaking the electrolyzing circuit. This method of control entirely prevents the electrolyzers from discharging to the generator *A*, with the consequent possibility of polarity changes, if, through error or deliberately reversing electrical connections, the direction of flow of electrical current is changed. The smallest fraction of a reversed current through the shunt *N* brings the polarized relay into play, breaking the contact in the contactor switch *J* which, in turn, breaks the current through the coil of the potential relay *E*, thereby releasing the connection *G* and breaking the circuit *G*, which drops out the magnetic contactor

\* U. S. Patent No. 1,201,526, Oct. 17, 1916, to Swartley and Larsen.

*F* which interrupts the main electric circuit to the electrolyzers. This makes it absolutely impossible to operate on a reverse polarity.

The overload relay is manually operated and is calibrated slightly in excess of the normal operating amperage. In case of opening of the circuit, due to overload,

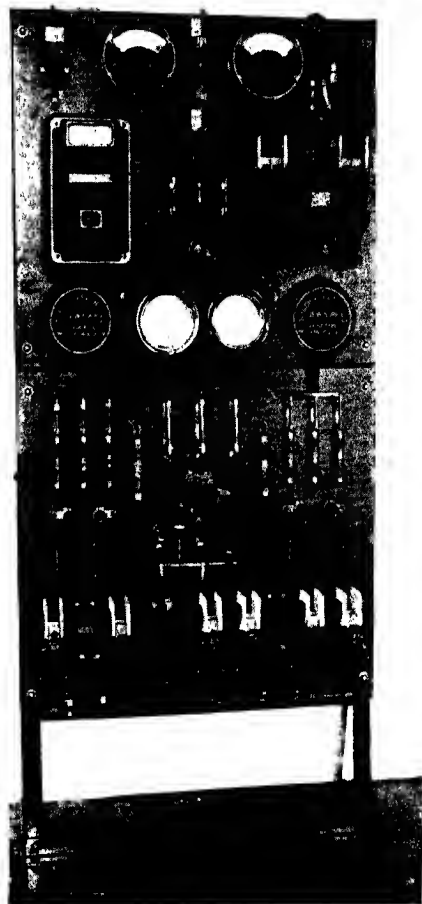


FIG. 139s.

it will be noted that the overload relay *M* will have to be reset by hand before the electrolyzing circuit can again be established.

Under normal operating conditions the ground detector lights *Q* will glow slightly but in case of a ground on one or both legs of the electrolyzing circuit, either or both of the lamps will glow brilliantly, showing the ground to exist.

**Jones \*** has designed an electrolytic cell for the production of hydrogen and oxygen. The apparatus is provided with a number of electrodes, and a diaphragm between adjoining electrodes forms chambers for the separation of the evolved gases, with gas ducts leading from them and separate conduits connected with the gas ducts. The electrolyte is conveyed to the several chambers by supply ducts connected to a supply conduit, the various conduits being located beyond the electrodes, and so arranged as to be outside the path of the electric current through the apparatus. A simple form of electrolytic cell for the production of oxygen and hydrogen is proposed by **Shaw.†** The positive electrode is readily removable without disturbing the other parts. **Hepburn ‡** has designed a bipolar electrode generator. §

**Jaubert ||** recommends a type of electrolytic hydrogen generator having electrodes covered by bells brought near to each other to diminish the resistance. The active surface of each electrode projecting below the lower level of the bell is inversely proportional to the volume of gas liberated at each electrode, while the volume of each bell is directly proportional to the volume of gas liberated. The bells are provided with cocks, or outlet collectors for the gases, and with insulated sleeves for the cables connected to the electrodes.

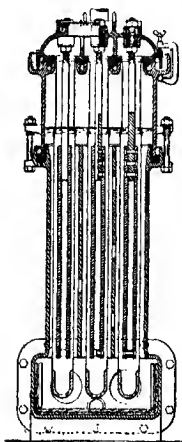


Fig. 139.

**Mueller and Rowlands ¶** describe a water electrolyzing apparatus made as follows:

A tank (Fig. 139) is made in two sections, a lower and an upper section, electrically separated by an insulating joint formed by a trough extending around the top of the lower section and containing a U-shaped insulating gasket of soft rubber which forms a cushion and also a hermetic seal. A liquefiable insulator such as paraffin filling the upper portion of the trough further insures a tight joint between the sections. The lower edge of the upper section rests in the groove of the gasket. The interior of the lower section is divided by longitudinal webs parallel with the side walls, into equal-sized cellular spaces which are open at top and bottom, these webs extending only from the upper edge of the section to the top of the enlarged base. The webs are perforated at intervals with holes. The anodes (three in number) are disposed in the spaces between the webs and side walls of the section thus exposing a double surface to the electric current

\* U. S. Patent No. 1,212,229, Jan. 16, 1917; J. S. C. I., 1916, 391.

† U. S. Patent No. 1,208,722, Dec. 12, 1916.

‡ British Patent No. 12,730, 1915; U. S. Patent No. 1,213,871, Jan. 30, 1917; J. S. C. I., 1916, 1120.

§ A description of the Frazer Generator is found in U. S. Patent No. 1,262,034, April 9, 1918.

|| British Patent No. 102,974, Dec. 28, 1916; J. S. C. I., 1917, 602. See also U. S. Patent No. 1,255,096, Jan. 29, 1918.

¶ U. S. Patent No. 1,220,262, Mar. 27, 1917.

for each anode, and hang in diaphragms of woven asbestos. The lower section is the negative electrode, while the upper section is insulated from both electrodes and is designated the neutral section. The anodes are suspended from the cover which in turn rests upon the neutral section but is insulated therefrom by means of a grid-shaped rubber gasket. To insure gas-tight joints between the hydrogen and oxygen chamber, and for sealing both chambers from the outer air, the neutral section is provided with a series of parallel inner troughs for the former, and for the latter is provided with an encompassing outer trough in which the depending marginal flange of the cover is sealed by paraffine wax or pitch. The diaphragms each consist of two parts, the diaphragm proper and a hanger. The hanger is made of thin sheet metal, and obviates the necessity of rendering gas-impermeable that portion of the diaphragm which extends above the liquid level. It is tubular in form, of the same cross-section as the diaphragm and of sufficient length to extend below the liquid level. It is formed at its upper end with an outwardly and downwardly projecting flange of proper form to fit into the sealing trough which extends continuously around each hanger. The cell represents a highly elaborated form of water electrolyzing apparatus the complete details of which cannot be presented here. Another form of apparatus designed by Mueller and Rowlands \* consists of a deep metal tank divided into communicating compartments by vertical partitions which form, with the sides, a series of electrodes of the same polarity. The tank has an arched metal cover from which depend a number of metal plates, one nearly to the bottom of each compartment, forming a corresponding series of electrodes of opposite polarity. The cover is insulated from the tank by a diaphragm through openings in which the metal plates extend; and each plate is surrounded by a tube of flexible, non-corrodible material †

According to Sebille,‡ hydrogen and oxygen are generated electrolytically, then cooled as they pass from the generator into separate containers, the condensed moisture being led back into the generator. A diaphragm is so arranged, containing chambers through which the gases pass on their way to their respective containers, that a predetermined difference of pressure on one side of the system causes the diaphragm to close the gas entrance to the opposite container, until a balancing pressure has again been raised on that side. By means of a body of water the gases are automatically compressed to a pressure higher than that originally generated. Sebille § also describes a system of gas storage chambers having automatically-controlled valves regulating the flow of gases.

¶ method for the electrolysis of water to produce hydrogen forms the basis of Japanese Patent 30,437 of Dec. 4, 1916, by the Yokohama Fish Oil Co. || The apparatus is provided with means for collecting hydrogen and oxygen completely separated from each other.

In a form of electrolytic cell for obtaining hydrogen and oxygen, described by Churchill & Co., and Geeraerd,¶ a vertical series of inclined non-conducting vanes are arranged close to the electrodes to confine gas flow to the space between the vanes and the electrodes.

\* U. S. Patent No. 1,219,843, Mar. 30, 1917.

† See also U. S. Patent No. 1,221,206, Apr. 3, 1917.

‡ U. S. Patent No. 1,230,803, June 19, 1917.

§ U. S. Patent No. 1,222,809, Apr. 17, 1917; also describes a system of gas storage chambers having automatically controlled valves regulating the flow of gases.

|| Chem. Abs., 1917, 1932.

¶ British Patent No. 101,598, May 11, 1916; Chem. Abs., 1917, 122.

## CHAPTER XXVII

### PRECAUTIONS IN HANDLING HYDROGEN. SAFETY DEVICES. PURIFICATION OF GAS

The handling of electrolytically-derived gases brings with it the possibility of explosions due to accidental mixing of the two gases, and to guard against serious results, at frequent intervals in the connections of the apparatus and service pipes, safety devices should be inserted.

The common form of safety device is the wire-gauze arrangement of **Sir Humphrey Davy**. It usually consists of a roll of wire gauze inserted in the pipe connections. Such arrangements sometimes will check the progress of an explosion temporarily or completely, but as a rule when an explosion wave passes along the pipe in which the wire gauze is placed, although checked temporarily by the wire-gauze obstruction, it soon heats the latter to the ignition point. Thus the gas on the other side of the gauze is ignited and the explosion wave continues on its course.

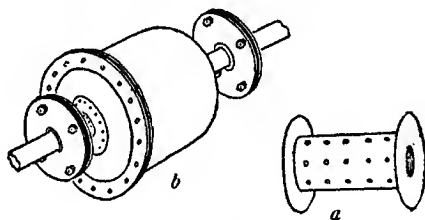


FIG. 140.

When wire gauze is used preferably it should take the form shown in Fig. 140. A spool *a* carries perforations along its stem and over this wire gauze is wound to make a thick layer. The spool is placed in the holder *b* and fitted tightly in place against a rubber gasket so that gases entering one end of *b* will pass along the hollow stem, flow through its perforations and those of the gauze and make their exit at the opposite end of *b*.

Glass wool obstructs explosion waves in a fairly satisfactory manner if it is inserted into the pipe connections in such a way as to fill the cross-sectional area without being packed so tightly as to greatly

reduce the flow of gas. Layers of glass wool, or finely-divided refractory material, such as fire-brick granules of about 20 mesh, alternated with bundles of wire gauze, may be packed into pipes of relatively large diameter to form an excellent safety device, which is rendered even more reliable if placed in a tank of water so as to be kept cool in event an explosion wave causes ignition of the gas at the surface of the outer layer.

It is stated by **Schoop** that under the conditions occurring in practice explosion mixtures are formed when either gas contains by volume 6 to 8 per cent of the other gas. Such an impurity may quite readily occur through injury to the diaphragm of cells of the asbestos-diaphragm type, and in constructions similar to the Garuti cell care should be taken to prevent an excess voltage which will render the diaphragms bipolar.

Boynton's device for preventing the transmission of explosions is shown in Fig. 141. *A* is the gas inlet, *B* the outlet, *E* one or more perforated plates and *H* a space filled with fragments of metal.\*

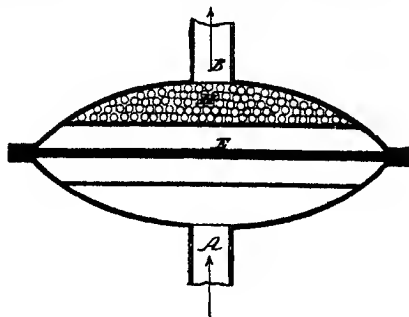


FIG. 141.

For the prevention of hydrogen explosions steel wool is recommended by **Ohmann**.† He regards steel wool as very suitable to take up and carry off the heat developed and, by lowering the temperature in this way, preventing the spreading of an explosion. To insure against the danger of an explosion, a roll of the wool, somewhat tightly pressed together, is placed in the gas conduit. Trials with a mixture of  $\frac{2}{3}$  hydrogen and  $\frac{1}{3}$  air, also with the strongest explosive gas mixture  $2\text{H} + \text{O}$ , showed that the explosive flame or wave was checked and extinguished in contact with the wool.

\* U. S. Patent 58,055, Sept. 18, 1866. See also U. S. Patents 713,421, 730,807, 743,064, 819,202 and 948,323.

† Z. physik. chem. Unterricht, 11, 272; Chem. Zentr. (1912), 1, 1426.

The various possible causes of certain fatal accidents resulting from the explosion of oxygen or hydrogen cylinders has been discussed by **Bramkamp**.\*

In most cases it is certain that an explosive mixture of hydrogen and oxygen has been introduced into the cylinder. The two most



FIG. 142. High-pressure cylinders for hydrogen.

important causes of this are: (1) the use of the same compressor alternately for both gases; and (2) unsatisfactory control and attention when the gases are obtained at the same time in the electrolysis of water. Other causes which may contribute but which are unlikely in themselves to account for an explosive mixture in a full cylinder are: (1) the use of an oxygen cylinder as a hydrogen cylinder or vice versa, without previously removing all the original gas; and (2) the absorption of hydrogen by finely-divided iron inside the cylinder. The various methods by which the explosive mixture when present may be exploded include: (1) ignition of oil or other combustible

material in the valve or pressure gauge by the compressed oxygen; (2) local rise in temperature of the gas due to sudden closing of the valve; (3) catalytic action of finely-divided iron in causing combination in the mixture and raising its temperature; and (4) pyrophoric oxidation of finely-divided iron. **Bramkamp** is of the opinion that with suitable precautions an explosive mixture need never be put into a cylinder, and that all cylinders should be tested by analysis of their contents immediately after filling.

Tubes of compressed hydrogen, accidentally contaminated with air, have been known to explode on connecting them with a manometer for the purpose of measuring the pressure of the gas. **Lelarge** † has found that if ordinary manometers are employed in the usual way, such explosions may occur whenever the hydrogen contains enough air to render it explosive, and the pressure is sufficiently high. The reason probably lies in the rise of temperature produced by the sudden

\* *Zeit. ang. Chem.* (1912), 536.

† *Compt. rend.* (1912), 914.

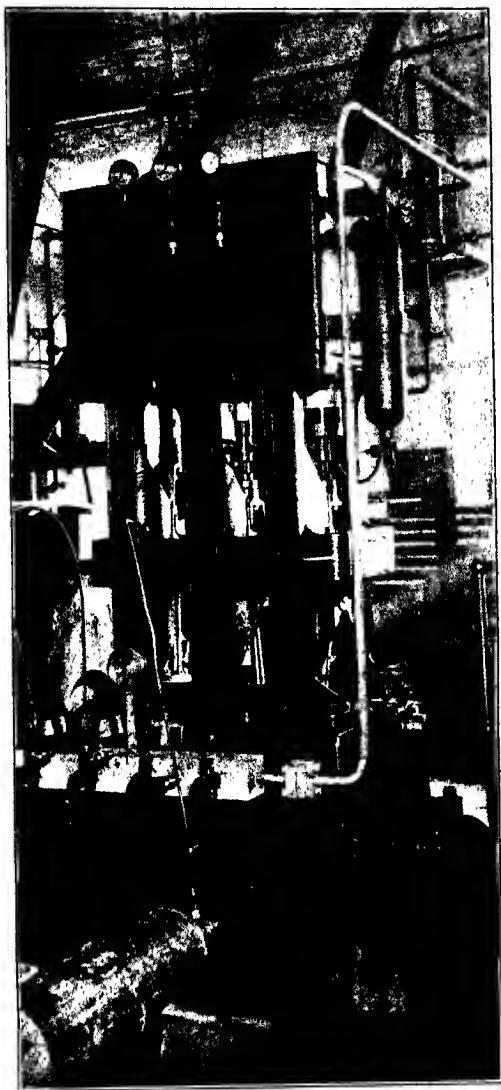


FIG. 143. Compressor for compressing hydrogen or oxygen into cylinders.



and more or less adiabatic compression of the air in the manometer. Such accidents may be avoided by interposing, between the tube of compressed gas and the manometer, a safety-tube containing discs of metallic gauze of such mass that they are not appreciably heated by combustion of the gas mixture in the manometer. By this means the ignition of the main body of gas is prevented. Similar safety-tubes should be employed whenever a highly-compressed explosive gas mixture is allowed to expand suddenly into a confined space. Before measuring the pressure of compressed hydrogen, liable to contain air or oxygen, it is advisable to determine its density, as a further safeguard.

#### SUMMARY

The majority of the numerous proposals for making hydrogen in various ways have been outlined in the foregoing for the reason that many investigators at the present time are studying the subject of hydrogen generation, and everywhere present and prospective users of hydrogen are seeking information which may enable a better understanding of the subject.



FIG. 144. Pressure tank for storage of hydrogen.

For oil hydrogenation at least four methods of generating hydrogen are likely to find a place. These are the (1) steam-iron, (2) water-gas liquefaction, (3) water-gas and lime and (4) electrolytic systems. With the exception of the latter these all require a water-gas plant with a not wholly simple system of purifiers, etc. As to the steam-iron method it may be noted that the opponents of this system claim it has been shown in practice that the iron sponge will not regenerate after a few operations and the iron retorts used are demolished all too soon by the high heat employed and have to be continually replaced. The advocates of the system claim great improvement in the matter of longevity of the iron sponge and also figure on a cost of production

around 90 cents to \$1.00 per 1000 cubic feet of hydrogen. It is doubtful if this figure generally could be reached and so far as the author can ascertain the cost in this country with plants of moderate size is approximately \$1.50 per M. The liquefaction system, although scarcely feasible to install in a small way, should prove attractive for large scale operation as the cost of production is not over \$1.00 to \$1.20 per M for gas of very fair purity. The objection has been raised that the by-product of carbon monoxide under high pressure is dangerous to handle. The water-gas and lime system from the point of view of low cost of operation has much in its favor, but has as yet received no extensive technical application. The electrolytic process may be called the foolproof system, as with proper safeguards against mixing of the gases and suitable safety devices, the generating plant may be operated with unskilled labor. The objections raised against it are the floor space required and the high cost of the gas. If, however, the oxygen is saved and compressed it can usually be sold at a profit which, credited against the hydrogen account, greatly reduces the cost of the latter. For small plants electrolysis has much in its favor.\*

#### PURIFICATION OF HYDROGEN

In the previous discussion of methods of producing hydrogen various procedures of purification have been mentioned. To summarize,

\* The cost of hydrogen per cubic meter (1 cubic meter = 35.3 cubic feet) produced in various ways is given by Sander (*Zeitsch. f. angew. Chem.* (1912), 2407) as follows:

##### *Stationary Plants*

	Cents
Acetylene (Carbonium).....	3½
Steam (Internat. Wasserstoff).....	2½-5
Water gas (Griesheim-Elektron).....	1½-2½
Water gas (Linde-Frank-Caro).....	2½-3½
Oil gas (Rincker and Wolter).....	2½-3½

##### *Portable Plants*

	Cents
Iron and sulfuric acid .....	12½-20
Aluminium and caustic soda.....	about 62½
Silicon and caustic soda.....	17½-20
Ferro-silicon and caustic soda.....	17½-20
Calcium hydride.....	about \$1.00
Hydrogenite (Jaubert).....	about 37½
Maricheau-Beaupre system .....	about 37½
Activated aluminium (Griesheim-Elektron).....	about 45

Sachs (*Zeitsch. f. angew. Chem.* (1913), No. 94, 784) believes the cheapening of the cost of manufacture of hydrogen due to the demand for this gas in air ship practice is in part responsible for the rapid development of oil hardening processes.

oxygen may be eliminated by passing the gas through heated tubes containing copper turnings; carbon dioxide by exposure to hydrated lime, carbon monoxide by contact with soda lime at 300° C. or over, in the presence of moisture, or with acid cuprous chloride; and nitrogen may be removed by exposure to heated calcium carbide. Moisture may be reduced to a negligible amount by means of quicklime, calcium chloride or other desiccating agent.

Catalyzers of different types vary considerably in their resistance to impurities or catalyzer poisons in the hydrogen, but the period of activity of the more reliable catalyzers is at best all too short, and it may be laid down as a general rule that hydrogen free from moisture, oxygen, sulfur, phosphorus, chlorine, arsenic and cyanogen compounds should be employed. Of course there are exceptions to this, as, for example, with nickel oxide catalyzers oxygen is thought not to be detrimental and in fact by some is regarded as advantageous.

The *Badische Anilin und Soda-Fabrik* \* remove traces of carbon monoxide from hydrogen by passing the gases through caustic alkali solutions at high temperatures and pressures, e.g., hydrogen containing 1 per cent of carbon monoxide is treated with (a) an 80 per cent solution of caustic soda at 50 atmospheres pressure at 260° C., or (b) a 25 per cent solution of caustic soda at 200 atmospheres pressure at 240° C.†

Hydrogen prepared from commercial zinc and acid, is bubbled through petroleum spirit cooled by liquid air. A temperature of 110° C., according to *Renard*,‡ suffices to insure the removal in this way of all the arseniuretted hydrogen even from a rapid stream of the gas.

*Wentzki* removes arseniuretted hydrogen from impure hydrogen by passing the gas upwards through a cylinder packed with a mixture of two parts of dry chloride of lime and one part of moist sand or other inert material. If the column of purification material be sufficiently high, the whole of the arsenic is retained. A small quantity of chlorine is set free, but can be removed by passing the hydrogen through a second cylinder packed with nearly dry slaked lime.§

*Rabenalt* || purifies hydrogen by passing it into a solution of iodine through which an electric current is simultaneously conducted.

\* French Patent 439,262, Jan. 22, 1912.

† By heating a solution of caustic alkali under a pressure greater than five atmospheres, hydrogen is freed from sulfur and sulfur compounds. (*Badische*, British Patent 14,509, June 23, 1913.)

‡ *Compt. rend.* (1903), 136 (22), 1317.

§ *Chem. Ind.* (1906), 405.

|| *U. S. Patent* 1,034,646, Aug. 6, 1912.]

For purifying electrolytic gases **Knowles** \* uses the apparatus as shown in Fig. 145. The gas to be purified is first passed through an ordinary washer then through an explosion trap and finally enters the purifier proper. In its entry into the purifier the in-going gas is pre-heated by passage around the conduit through which the out-going gas and vapor is passing. In the purifying chamber the gas passes through contact material and water vapor is formed and is condensed and removed. In the illustration the web *k* supports grids *l* of porcelain on which the contact material is spread. Knowles states that when the apparatus is working properly no external heat is required on account of the rise in temperature caused by the condensation.

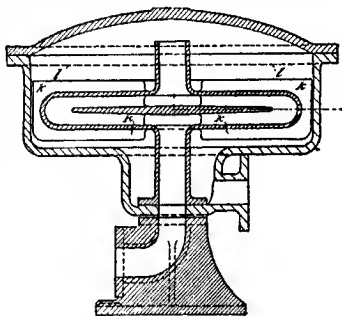
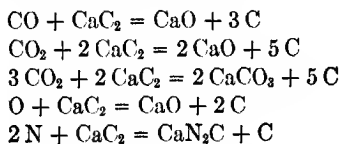


FIG. 145.

The removal of sulfur from gas by the **Carpenter** process † involves passing the gas over reduced nickel heated to 800° to 900° F. when carbon bisulfide reacts with hydrogen to form hydrogen sulfide and the latter body is absorbed in the usual manner.

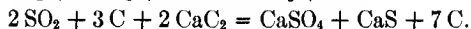
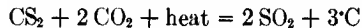
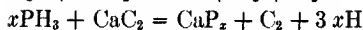
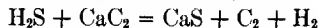
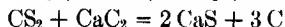
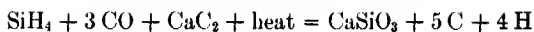
The treatment of water gas to separate pure hydrogen, as described by **Frank**, ‡ is of interest in this connection. Water gas, previously dried as much as possible, is conducted over calcium carbide, at a temperature from 300° C. up to the melting point of the carbide. When water gas is conducted over carbide thus heated an absorption of all the substances associated with the hydrogen takes place. Carbon monoxide or dioxide forms with the carbide, lime or carbonate of lime and carbon. The nitrogen is likewise absorbed. The hydrocarbons are decomposed when passed over the heated lime-carbon material with the separation of carbon. The action of the carbide on various gases is indicated by Frank in the following reactions:



\* U. S. Patent 1,073,246, Sept. 16, 1913.

† Jour. Ind. & Chem. Eng. (1914), 262.

‡ U. S. Patent 964,415, July 12, 1910.



Almost chemically pure hydrogen is ultimately obtained as the final product. Carbon monoxide or dioxide may be previously entirely or partially removed from the water gas by mechanical separation of the constituent gases to relieve the carbide from the duty of separating the major part of the gases. If the water gas is produced at a high furnace temperature and contains in addition to hydrogen almost exclusively carbon monoxide and only a little carbon dioxide, the mechanical separation is preferably effected by conducting the water gas, which has been suitably cooled, into a Linde's air-liquefaction machine or other similarly constructed apparatus to liquefy the carbon monoxide; the dioxide and small quantities of silicon-hydrogen, etc., being obtained solid, whereas the hydrogen remains gaseous and can be separated and conducted away. If the water gas is produced at a low temperature, and if little carbon monoxide and principally carbon dioxide are obtained in addition to hydrogen, the previous mechanical separation may be effected by the water gas being cooled down to a temperature below that of the congealing or liquefying point of the secondary constituents of the water gas (carbon dioxide, carbon monoxide, etc.), these secondary constituents being separated in this manner in a solid or liquid form from the hydrogen which is obtained. After the previous mechanical separation of the secondary gases, the hydrogen which contains some remnant of other gases, as CO, CO<sub>2</sub>, SiH<sub>4</sub>, H<sub>2</sub>S, PH<sub>3</sub>, N, CS<sub>2</sub>, and hydrocarbons, is then subjected to a final purification by conducting it over carbide. Before being passed over the carbide, the water gas may be freed from carbon dioxide and monoxide by treatment with lime and cuprous chloride solution respectively.\*

**Bosch and Wild** † have found that by treating hydrogen under pressure exceeding five atmospheres with a hot solution of fixed caustic alkali, sulphur and compounds containing sulphur can be practically completely removed.

The concentration of the alkaline solution and the temperature and pressure employed can be varied within wide limits. As an example, caustic soda solution

\* French Patent 371,814, Nov. 26, 1906.

† U. S. Patent No. 1,133,087, March 23, 1915.

of from 10 to 50 per cent can be employed at a temperature of from 150° to 225° C. and a pressure of fifty atmospheres. As a rule, if higher pressures be employed, the gases can be passed through the caustic alkali solution with a greater velocity while still effecting a total separation of all sulphur and sulphur compounds.

A purifier for separating dust and sulphur compounds from producer gas, water gas, and the like is described by **Berlin Anhaltische Maschinenbau \*** as follows: Within and spaced away from the wall of the purifier is a retort packed with turnings of iron or other metal capable of combining with sulphur compounds. Except at the two ends the wall of the retort is porous. The gas enters the purifier, and passes through the porous wall of the retort, which retains dust, etc. A blast of air may be passed into the purifier to bring it to and maintain it at the requisite temperature for the retention of the sulphur compounds by the iron turnings.

It is stated by the **Badische Company †** that carbon monoxide can be very quickly and effectively removed from gas mixtures by means of ammoniacal cuprous chloride solution under pressure.

The solutions contain, in 1 liter, considerably more than 60 grams of ammonia gas in the form of free base or carbonate. Iron apparatus or parts in motion are not injured by this solution so that high pressure can be employed, where stone-ware and lead are not suitable. Ammonia is supplied as it is lost, the solution is kept in circulation between the absorption and a lower pressure chamber where the carbon monoxide is removed, and any oxidation of copper is corrected by the carbon monoxide before it is removed. A suitable solution is prepared by mixing 200 kilograms of cuprous chloride, 250 kilograms of ammonium chloride, 500 kilograms of 25 per cent ammonium hydroxide and 500 kilograms of water. Operating at pressures above 100 atmospheres very small amounts of carbon monoxide may be removed from gases (such as hydrogen containing carbon monoxide) in a short time.

The absorption of carbon monoxide from oxygen-free gas mixtures by ammoniacal cuprous chloride solutions is carried out by the **Badische Company ‡** with an addition of oxygen to the gas sufficient in amount to prevent the separation of copper but not in such a quantity as to cause any marked oxidation of carbon monoxide.

A method of freeing gases from carbon dioxide present as impurity is given by **Soc. L'Air Liquide, §** which consists in subjecting the impure gas first to a physical purification by solution under pressure in water and then to a chemical purification by the action of purifying reagent dissolved in the water.

The process is applicable to the removal of carbon dioxide from water gas or water gas modified by catalysis or by passage over hydrated lime, prior to liquefaction of the gas. The process is effected by bringing the compressed gas into contact with a counter current of water in a tower, at the upper portion of which is

\* German Patent No. 271,122, Dec. 12, 1912; U. S. Patent No. 1,129,558; J. S. C. I., 1914, 472.

† German Patent No. 282,505, Nov. 19, 1913; Chem. Abs., 1915, 2299; see also British Patent No. 9,271, Apr. 14, 1914.

‡ Chem. Abs., 1917, 873; Austrian Patent No. 72,240, Aug. 10, 1916.

§ British Patent No. 15,053, June 23, 1914.

introduced a small quantity of a lime or caustic soda. The dissolved gas may be subsequently removed from the liquid by relieving the pressure thereon, and, when lime is used, the precipitated carbonate may be filtered off and the water returned to the tower.

In a process for the absorption of gases by liquids, under pressure, with subsequent regeneration of the absorbent by relieving the pressure, **Ges für Lindes Eis maschinen** \* absorption is effected under as high a pressure as possible and the absorbed gas subsequently released by producing a partial vacuum in the absorption vessel and simultaneously passing through it a current of gas in which the concentration of the absorbed gas, if this be present, is lower than corresponds to its partial pressure, in the gas above the solution. It is stated that by this process the absorption of carbon monoxide in cuprous chloride solution, which hitherto has proved impracticable, may be used with good results, e.g., for the production of hydrogen free from carbon monoxide.

**Knowles** † has devised an apparatus for the purification of electrolytic gases, consisting of a chamber in which is located a web of metal or other material coated with a catalytic agent, and heated either by electricity or other suitable means. The design is such that the gases have a long space to travel in contact with the catalytic material and are thus well purified.

To remove oxygen from gaseous mixtures, **Siemens and Halske** ‡ pass the gases over a metal heated to incandescence, the metal being one, such as zirconium or titanium, the oxide of which is not reduced by hydrogen or carbon monoxide at the temperature of working. In practice gases to be freed from oxygen frequently contain hydrogen or oil vapors. By the process described, it is stated that oxygen can be removed from such gases without formation of steam.

**Ueno and Kimura** § purify by-product hydrogen by treatment with metallic copper, a cuprous salt and ammonium hydroxide, with or without the addition of another ammonium compound. **Ueno** || employs colloidal platinum, palladium, iridium or osmium in an aqueous vehicle containing an organic body such as sugar or glycerine, gum arabic and soap.

When working with hydrogen at raised temperature and under pressure in iron vessels, according to **Bosch**, ¶ if the iron contains carbon the strength of the vessel suffers to such an extent that after a very short time it is no longer able to withstand the higher pressure which is being employed, due to the action of the hydrogen upon the carbon. The use inside such iron tube of a lining which is chemically not acted upon by hydrogen is of little value, since, when high temperatures are employed, practically all substances are pervious to hydrogen under pressure. Although the quantity of hydrogen which diffuses through the walls of the tube is only minute

\* German Patent No. 289,106, Mar. 29, 1914; J. S. C. I., 1916, 523.

† U. S. Patent No. 1,073,246, Sept. 16, 1913.

‡ German Patent No. 279,132, June 28, 1913; J. S. C. I., 1915, 230.

§ Chem. Abs., 1918, 208; Japanese Patent No. 31,202, July 10, 1917.

|| Japanese Patent No. 31,291, July 10, 1917.

¶ U. S. Patent No. 1,188,520, June 27, 1916.

in comparison with the total quantity of gases treated in such tube, yet in course of time this small quantity is sufficient to act on the carbon contained in the iron of the tube to such an extent as to deteriorate the resisting power of the tube.

Bosch states that he can work conveniently with flowing hydrogen under continuous pressure and at raised temperatures if the vessel in which the reaction is being carried out and within which the high pressure is being maintained, be surrounded by some kind of structure which is capable of supporting the inner vessel, but which itself readily allows any gas to escape which may diffuse through the walls of the inner vessel. This can be effected by surrounding the inner vessel with a series of steel rings, or a suitable network of bars, or the inner tube may be covered with a second tube which is perforated, the essential condition being that the outer tube, which is supporting the inner tube, is not impervious to the hydrogen which diffuses through the inner tube at the high temperature and pressures employed. It is most convenient to construct the outer perforated tube, network or rings, of steel, while the inner tube, in which the hydrogen is contained under pressure and heat, may be constructed either of steel, or of some material which does not contain carbon, such as wrought iron (practically free from carbon), nickel or silver.

Reactions in which hydrogen is involved under pressure and at high temperatures are carried out in an apparatus comprising an exterior (metallic) receiver, capable of supporting the pressure, and an interior receiver (e.g., of glazed porcelain, glass, quartz, etc.), capable of resisting the chemical action and the diffusion of the hydrogen. Or, the reaction is allowed to take place in an inner metallic or non-metallic porous receiver, which is separated from the outer wall, supporting the pressure, by an alloy or composition capable of resisting the chemical action and diffusion of the hydrogen.\*

Pier † describes an apparatus for effecting reactions with hydrogen under pressure. To prevent leakage of hydrogen, a layer of molten Wood's metal or other readily fusible alloy is maintained between the upper wall and the outer casing of the vessel (which may be of steel). The inner wall may be of porcelain or metal. The apparatus will withstand 150 atmospheres pressure without leakage.

#### EFFECTS OF THE PRESENCE OF HYDROGEN IN ELECTROLYTIC OXYGEN

Experiments conducted by the Bureau of Mines indicate that, at atmospheric pressure, mixtures of oxygen and hydrogen containing less than 10 per cent by volume of hydrogen are inflammable but not explosive. Teras and Plenz find at least 30 per cent of oxygen is required for explosion. The electrolytic industry for making oxygen and hydrogen, as a general rule, attains on an industrial scale the generation of both oxygen and hydrogen at purities well above 99 per cent. Oxygen containing but 1 per cent of hydrogen is a non-

\* Chem. Abs., 1915, 28; French Patent No. 469,391 and First addition, March 7, 1914.

† U. S. Patent No. 1,159,865.



hazardous product, as the hydrogen in such a mixture cannot be made to combine with the oxygen to produce an explosive reaction. Hydrogen containing but 1 per cent of oxygen is likewise in itself a safe product, as the oxygen in such a mixture cannot be made to combine with the hydrogen to produce an explosive reaction.

The attention of the Bureau of Mines \* has been directed to a series of explosions of oxygen made by the electrolytic process in which life has been lost, as a result of hydrogen being mixed with oxygen. Rice, of the Bureau of Mines, reports that this is due to improper design in the manufacturing apparatus, i.e., the cells and electrical connections; to insufficient safeguards connected with the electric apparatus, the polarity suddenly and unexpectedly shifting; to the manufacture of oxygen without frequent analyses; and to incompetent or ignorant attendants. Unfortunately, certain makers of oxygen-manufacturing apparatus have advertised that any laborer can take care of their apparatus. It is believed that the manufacture of electrolytic oxygen can be carried on in a manner to make it entirely safe. Nevertheless, certain tanks from one batch caused three widely separated explosions in California, killing seven men in all, and an analysis of gas from a tank filled at the same time showed that it contained over 50 per cent of hydrogen.

The California Commission limits hydrogen content in oxygen containers to 2 per cent after thorough investigation as to the cause of three explosions.†

Wohler ‡ referring to the regulations which have been enforced in Germany since 1902 with regard to the filling and use of compressed gas cylinders for oxygen and hydrogen gases, gives details of some recent explosions to show that in spite of all these precautions accidents due to carelessness and negligence are of frequent occurrence.

The most disastrous of these, in which three men were killed and many were injured, occurred at Darmstadt. An empty oxygen cylinder of 210 cu. ft. capacity was filled with hydrogen, but the error was discovered before the gas was used and the cylinder was returned to the compressed gas works. Without emptying the cylinder, the men in charge of the oxygen-filling machinery filled the cylinder to its maximum capacity with oxygen, and when the cylinder arrived at the railway workshops the second time, and was put into use, it burst. The author points out that owing to the shortage of copper the connecting gas couplings used at the filling works are now of iron or steel. The rule with regard to right- and left-handed threads to the cylinder fittings for the different gases is, therefore, easily evaded, for a steel or iron screw may be externally threaded on a brass connecting piece whatever the thread

\* Met. Chem. Eng., 1917, 402.

† Brownell, Eng. Record, 1917, 594.

‡ Z. angew. Chem., 1917, 30, 174; J. S. C. I., 1917, 917.

may have been on this originally. The regulations with regard to the use of distinctive colors for the cylinders containing the two gases have also been often ignored lately, owing to labor shortage and similar difficulties, and cylinders have been used indiscriminately for oxygen or hydrogen, without regard to their color or markings. As a precaution against similar accidents and explosions Wohler recommends the application of the Haber test for explosive gases before the gas from any cylinder is used, or the still more simple soap-bubble test, which consists in blowing a bubble with the gas from the cylinder, and then applying a light. These tests, however, are of little value if left in the hands of the workmen, since negative results can easily be obtained with them.

**Hammond** \* describes an apparatus that prevents polarity reversal by use of an automatic switch which completes the connection with the cells only when the normal speed of the generator is reached. Reversal of phase is prevented by use of a polarized relay connected to a special shunt which provides for a single-pole relay in the control circuit. Apparatus for the determination of purity of oxygen by absorption with metallic copper and of hydrogen by the combustion method are illustrated. Causes of explosions and precautions to be observed are given.†

The Underwriters' Laboratories (207 E. Ohio St., Chicago, Ill.) have in preparation Tentative Standards for Oxygen and Hydrogen for Industrial Uses and for Electrolytic Oxygen and Hydrogen Plants and Their Operation. In the compilation of these standards the Underwriters' Laboratories have had the assistance of the Standards Committee of the Electrolytic Oxygen and Hydrogen Association, formerly Gas Products Association (29 South La Salle St., Chicago, Ill.), and the Committee on Electrolytic Oxygen and Hydrogen of the Compressed Gas Manufacturers' Association (120 Broadway, New York City), and after further revision it is expected these standards will be adopted by electrolytic oxygen and hydrogen manufacturers of this country.‡

\* Machinery, **23**, 1070, 1917; Chem. Abs., 1917, 2860.

† An explosion arrester involving the use of a water seal is described by Ellis, U. S. Patent No. 1,170,055, Feb. 1, 1916.

Oil-hardening tank explosion. (Byrne, Chem. Trade J., 58, 164 (1916); Chem. Abs. 10, 1271.) An explosion occurred May 22d, 1915, in one of six tanks employed by Messrs. Ardol, Ltd., Selby, Yorks, in converting oil into a solid by means of hydrogen. Each tank was fitted with 3 vertical coils of copper tubing forming an endless circuit through which hot water was passed. Its temperature normally was about 290° and its pressure 2000 lb. per square inch. The oil in the tank was heated to a temperature of about 260° and the hydrogen, at a pressure of 5 lb. per square inch was sent from the bottom upward through the tank to the cleansing plant. The accident is found to have been due to a leakage from the copper coil producing an undue pressure in the tank.

‡ J. S. C. I., 1918, 251 R.



## APPENDIX A

### HYDROGENATED OIL PATENT LITIGATION

The general interest awakened by litigation in England over the Normann patent, together with the fact that the testimony given has brought out much of interest to investigators in the hydrogenation field, has led to the inclusion of a report of the Court proceedings which is here given substantially as published in the British Official Journal.

IN THE HIGH COURT OF JUSTICE. — CHANCERY DIVISION

Before MR. JUSTICE NEVILLE

Feb. 20 — Mar. 18, 1913

\* JOSEPH CROSFIELD & SONS LD. v. TECHNO-CHEMICAL  
LABORATORIES LD.

*Patent. — Action for infringement. — Admissibility of expert evidence. — Construction of Specification. — Insufficiency of Specification — Patent held invalid. — Action dismissed. — Costs on the higher scale allowed.*

*In 1903 a Patent was granted for a "Process for converting unsaturated fatty acids or their glycerides into saturated compounds." The process consisted in treating the fatty bodies with hydrogen in the presence of a finely-divided metal, such as platinum, iron, cobalt, copper, and especially nickel, adapted to act as a catalyzer. The Specification stated that the saturation might be effected by causing vapours of fatty acid together with hydrogen to pass over the catalytic metal, but that it was sufficient to expose the fat or fatty acid in a liquid condition to the action of hydrogen and the catalyst. The Specification gave no details of the process, but after having given, in general terms, an example of the process, stated that the quantity of the nickel added and the temperature were immaterial, and would only affect the duration of the process. In an action for infringement of the Patent, the Plaintiffs contended that the publication of the fact that the process could be carried out with bodies in the liquid state*

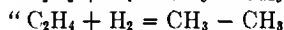
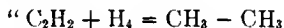
\* Supplement, June 18, 1913. The Illustrated Official Journal (Patents), Vol. XXX. Reports of Patent, Design and Trade Mark Cases. No. 12.

was of great merit; they claimed that the Patent was for a principle, and that, the Patentee having shown one way of putting it into practice, he was entitled to claim for all ways. The Defendants contended that the experiments of their witnesses showed that, for the success of the process, the catalyst must be prepared in a particular way and the process carried out with precautions not indicated in the Specification and requiring research for their ascertainment.

Held, that the Patentee claimed the hydrogenation of all unsaturated fatty acids, and their glycerides, by the use of finely-divided platinum, iron, copper, and cobalt, as well as nickel, and that if the process failed as to any of the bodies to be hydrogenated or any of the catalysts the Patent was invalid; that no method of carrying the alleged invention into effect was sufficiently described in the Specification; and that the Patent was invalid. The action was dismissed with costs.

On the 21st of January 1903 Letters Patent (No. 1515 of 1903) were granted to *Wilhelm Normann* for a "Process for converting unsaturated fatty acids or their glycerides into saturated compounds."

The Complete Specification was as follows:— "The property of finely-divided platinum, to exercise a catalytic action with hydrogen, as it does with oxygen, is already known. For instance, *Wilde* observed the following reaction taking place in the presence of platinum black:—



"and *Debus* noticed the reaction:



"Recently *Sabatier* and *Senderens* have discovered that other finely-divided metals will also exercise a catalytic effect on hydrogen, viz. iron, cobalt, copper and especially nickel. By causing acetylene, ethylene, or benzene vapour in mixture with hydrogen gas to pass over one of the said metals, the said investigators obtained from the unsaturated hydrocarbons saturated hydrocarbons, partly with simultaneous condensation.

"I have found, that it is easy to convert by this catalytic method unsaturated fatty acids into saturated acids. This may be effected by causing vapours of fatty acid together with hydrogen to pass over the catalytic metal, which is preferably distributed over a suitable support, such as pumice stone. It is sufficient, however, to expose the fat or the fatty acid in a liquid condition to the action of hydrogen and the catalytic substance. For instance, if fine nickel powder obtained by reduction in a current of hydrogen, is added to

“chemically pure oleic acid, then the latter heated over an oil bath, and a strong current of hydrogen is caused to pass through it for a sufficient length of time, the oleic acid may be completely converted into stearic acid. The quantity of the nickel thus added and the temperature are immaterial and will only affect the duration of the process. Apart from the formation of small quantities of nickel soap, which may be easily decomposed by dilute mineral acids, the reaction passes off without any secondary reaction taking place. The same nickel may be used repeatedly. Instead of pure oleic acid, commercial fatty acids may be treated in the same manner. The yellowish fatty acids of tallow, which melt between 44 and 48° C. and whose iodine number is 35.1, will, after hydrogenation, melt between 56.5 and 59° C., while their iodine number will be 9.8 and their colour slightly lighter than before, and they will be very hard.

“The same method is applicable not only to free fatty acids, but also to their glycerides occurring in nature, that is to say, the fats and the oils. Olive oil will yield a hard tallow-like mass; linseed oil and fish oil will give similar results.

“By the new method, all kinds of unsaturated fatty acids and their glycerides may be easily hydrogenised. It is not necessary to employ pure hydrogen for the purpose of the present invention; commercial gas mixtures containing hydrogen, such as water gas, may also be used.”

The Patentee claimed:—“1. The process for converting unsaturated fatty acids, or their glycerides, into saturated compounds, which consists in treating the said fatty bodies with hydrogen in the presence of a finely-divided metal adapted to act as a catalyser, substantially as described. 2. The herein described manufacture of saturated fatty compounds from unsaturated fatty acids, or their glycerides, by means of water gas or similar gas mixtures.”

On the 19th of December, 1911, *Joseph Crosfield & Sons Ltd.* commenced an action for infringement of the Patent against *Techno-Chemical Laboratories Ltd.* and *Nils Testrup*, claiming the usual relief.

The Plaintiffs by their Statement of Claim alleged that, (1) they were the owners of the Patent; (2) the Patent was valid and subsisting; (3) the Defendants had infringed and threatened and intended to infringe.

By their Particulars of Breaches they alleged that, (1) the Defendants had infringed by importing into, and by the manufacture, sale, offering for sale, supply and use in, this country of compounds made in accordance with the process described in the Specification and

claimed in both the Claims, and by the use in this country of the process; and (2), in particular, the Defendants, and each of them, had, on the 1st of December, 1911, caused to be treated with hydrogen in the presence of a finely-divided metal adapted to act as a catalyser, in their factory situate at "Fairlawn," Clapham Park, in the county of London, 9 kilogrammes of cotton oil, in infringement of both the Claims.

By their Defence the Defendants, (1) did not admit the allegations in paragraph 1 of the Statement of Claim; (2) denied that they, or either of them, had infringed or threatened or intended to infringe; and (3) said that the Patent was, and always had been, null and void.

By their amended Particulars of Objections they said that, (1) *Wilhelm Normann* was not the true and first inventor. (2) The alleged invention was not subject-matter for a valid Patent, by reason of the common and/or public knowledge at the date of the Patent. The Defendants would refer to all the prior publications set out in paragraph 4 below as disclosing part of the public knowledge. (3) The alleged invention was not useful. (4) The alleged invention had been published in this realm prior to the date of the Patent:— (i) By the deposit in the Patent Office Library of the following Specifications: (a) British:— *Lake* (No. 2798 of 1883) and *Ramage* (No. 7242 of 1901). (b) German:— *Zürer* (No. 62,407). The whole of each of the Specifications was relied upon. (ii) By the sale and publication in the United Kingdom, and by the deposit in the Patent Office Library, of (c) "Comptes Rendus de l'Académie des Sciences," of Paris, vol. 133, dated 1901, pages 321-4, comprising an article entitled "Chimie Organique. — Nouvelle méthode de préparation de l'aniline et des 'alcalis analogues.'" Note de MM. *Paul Sabatier* et *J. B. Senderens*. (d) "Bulletin de la Société de Chimie," series 3, vol. 1, pages 295-6, comprising a communication entitled "No. 29. — Transformation de 'l'acide oléique en acide stéarique'" by *De Wilde* and *Reychler*. (e) "Journal of the Chemical Society," London, for the year 1889, vol. 56, part 2, page 1140, comprising an abstract of the communication of *De Wilde* and *Reychler*. (f) "Watts's Dictionary of Chemistry," edition 1892, vol. 3, page 637, column 2, lines 42-4. (g) "Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften," Vienna, 1876, vol. 72, part II, pages 366-75; comprising a paper by *Guido Goldschmidt*, entitled "Über die Umwandlung von Säuren der Reihe  $C_nH_{2n-2}O_2$  in solche der Reihe  $C_nH_{2n}O_2$ ." (5) The Complete Specification of the Patent did not particularly describe and ascertain the nature of the invention and in what manner the same was to be performed, and was insufficient and/or misleading in the following par-

ticulars:—(a) No useful result could be obtained by following the directions given in the Specification. (b) No process was described by which, as alleged, saturation of unsaturated fatty acids, or their glycerides, could be easily or at all effected. (c) No process was described by which fatty acids, or their glycerides, could be hydrogenised by the action of catalytic iron, copper, cobalt, nickel or platinum. (d) No process was described whereby hydrogenation of fatty acids, or their glycerides, could be effected without the formation of secondary products. (e) No process was described whereby any useful results could be obtained by the use of any of the finely-divided metals mentioned. (f) No process was described whereby fatty acids, or their glycerides, could, as suggested, be hydrogenised by treatment in a vaporised condition. (g) The treatment as described of oleic acid in the liquid condition did not result in complete saturation, as alleged, or in any practical or substantially useful saturation. (h) No sufficient directions were given as to the quality of catalyst, or the temperatures or times required to produce the alleged results, or as to what variations of those factors might be required for different catalysts, and those factors were not immaterial as to the alleged results. (i) The same catalyst could not be used repeatedly as described at page 2, lines 40 to 41. Alternatively, no sufficient directions were given to enable the same catalyst to be used repeatedly. (j) No useful result could be obtained by the use of commercial gas mixtures as described on page 3, lines 5 and 6. (k) No sufficient directions were given as to the preparation of nickel or other metal to be used as catalyst. (l) The statement on page 3, lines 3 and 4, of the Specification, namely, that by the new method all kinds of unsaturated fatty acids and their glycerides might be easily hydrogenised, was incorrect. (m) No sufficient directions were given as to which impurities might be present with, or as to which impurities must be excluded from, the hydrogen in order that the process might be carried out.

By their further and better Particulars the Defendants alleged that as to paragraph 5 (l) of their Particulars of Objections, the following would not be easily or at all hydrogenised:—Olive, linseed, fish, whale, rape, and cottonseed oils, or any fatty oils; oleic, erucic, linolic, linoleic, and ricinoleic acids, or any unsaturated fatty acids, by treatment in a vaporised or liquid condition by the alleged new method. And they alleged as to paragraph 5 (m) that the following impurities must be excluded from the hydrogen in order that the latter could, by any process, hydrogenise fatty acids or their glycerides:—Sulphur, sulphuretted hydrogen, and all other volatile sulphur compounds, arsenic, arseniuretted hydrogen and all other volatile arsenic com-



pounds, phosphorus, phosphoretted hydrogen and all other volatile phosphorus compounds, chlorine, oxygen, the oxides of nitrogen, ammonia, and empyreumatic substances obtained in the production of water gas.

Upon an application by the Plaintiffs for further and better Particulars as to paragraph 5 (*l*), the Defendants alleged that no fatty oils and no unsaturated fatty acid could be easily or at all hydrogenised in a vaporised or liquid condition by the Plaintiffs' process, and stated that they did not intend to offer any evidence of specific instances other than those specified in the Particulars.

In their Answers to Interrogatories the Defendant Company stated that, on the occasion of the visit of the Patentee to the Defendant Company's premises at Fairlawn, Clapham Park, on the 1st of December, 1911, to inspect a process for the hardening of fats, there was used a cylindrical autoclave 1 metre high and  $\frac{3}{4}$  metre in diameter (inside measurements), with a steam jacket, and fitted with a non-conducting lining of unknown material. Nine kilograms of cotton oil were pumped into the autoclave, and 288 grams of a composition, containing a catalytic agent calculated on the oil, was used and was mixed with the oil prior to the introduction of the mixture into the autoclave. The autoclave was then filled with hydrogen from a cylinder to a pressure of 15 atmospheres. During the operation, the pressure varied from time to time according to the absorption of hydrogen. A mechanically driven circulation pump was connected with the autoclave both by its suction and delivery conduits. By means of a pump and a jet for spraying, a mixture of oil and composition containing the catalytic agent was drawn from, and forced back into, the autoclave. The iodine absorption was not determined. The composition containing the catalytic agent was prepared from a salt of nickel. The Defendant Company said that the catalyst was the subject of provisional protection (No. 4702 of 1912), and they objected to giving further particulars, but subsequently they said that the composition was prepared as follows:—About  $1\frac{1}{2}$  kilograms of nickel sulphate was dissolved in about 3 litres of water, and about the same weight of sodium carbonate, dissolved in about the same quantity of water, and at about 70–80° C., was added to the nickel sulphate which was at about 60–70° C. The mixture was stirred for about  $1\frac{1}{2}$ –2 hours, and the precipitate was filtered off and washed with distilled water at about 25° C. for 60–70 hours alternately in tanks and filter press. A small sample was dried and tested to ascertain that the precipitate had been sufficiently washed. The washed precipitate was dried in hot air at 80–85° C., and was calculated to weigh 720

grams. It was then roasted in an iron frying pan for about 15 minutes over an open Bunsen gas burner, and the weight after roasting was calculated to be about 380 grams. The product was heated to about 300° C. for about 6 minutes in a current of hydrogen in revolving glass tubes slightly inclined, the precipitate being introduced at the higher end and through a spiral glass tube, and the hydrogen at the lower end. The product, which weighed 288 grams, was directly introduced into a small quantity of oil, which was mixed with the 9 kilos the following day.

The Defendants during the trial referred to the following papers: — *Moissan*, Oxides of nickel ("Annales de chimie et de physique," 1880, 5th series, vol. 21, page 238) — the exhibit A.L. 9; *Moissan and Moureu*, Action of acetylene on iron, &c. ("Comptes Rendus," 1896, vol. 122, 1st half year, page 1240) — the exhibit A.L. 9; *Sabatier and Senderens* in the "Comptes Rendus" (the exhibit A.L. 5), Action of nickel on ethylene (124 (1897), page 616); Action of nickel on ethylene: synthesis of ethane (*ib.*, page 1358); Hydrogenation of acetylene in the presence of nickel (128 (1899), page 1173); Action of copper on acetylene; formation of a very condensed hydrocarbon, cuprene (130 (1900), page 250); Hydrogenation of acetylene in the presence of copper (*ib.*, page 1559); Hydrogenation of acetylene in the presence of reduced iron or cobalt (*ib.*, page 1628); Hydrogenation of ethylene in the presence of various reduced metals (*ib.*, page 1761); Hydrogenation of acetylene and ethylene in the presence of divided platinum (131 (1900), page 40); Action of various divided metals, platinum, cobalt and iron, on acetylene and ethylene (*ib.* (1900), page 267); Direct hydrogenation effected in the presence of reduced nickel; preparation of hexahydrobenzene (132 (1901), page 210); General method of synthesis of the naphthenes (*ib.* (1901), page 566); Hydrogenation of various aromatic hydrocarbons (*ib.*, page 1254); new method of preparing aniline and analogous alkalies (133 (1901), page 321); direct hydrogenation of carbon oxides in the presence of various divided metals (134 (1902), page 689); Hydrogenation of ethylenic hydrocarbons by the contact method (*ib.*, page 1127); Synthesis of various petroleum: contribution to the theory of the formation of natural petroleum (*ib.*, page 1185); Direct hydrogenation of acetylenic hydrocarbons by the contact method (135 (1902), page 87); Direct hydrogenation of oxides of nitrogen by the contact method (*ib.*, page 278); and a paper by the same authors in the "Annales de chimie," &c., 8th series, vol. 4 (1905), page 5 — an exhibit marked J.L. 1.

Sir A. Cripps K.C. for the Plaintiffs. — The Plaintiffs are substantially *Brunner, Mond & Co.*, and the real Defendants are *Lever Bros.*

*Ld.* An important feature of the invention is that it has enabled fish oils, and particularly whale oil, to be used for soap-making, hardening it and destroying its smell. Before the Patent, it was not known that the catalytic hydrogenation of fatty acids or oils could be effected without alteration of the quantity of oxygen contained in the acids or oils. The Patentee did not discover any new method of using catalysts, but he used them successfully with bodies with which they had never been used before; and he found that catalysts could be used with substances, that could not be readily vaporised, by simply treating them in the liquid state. That had been thought impossible. It is alleged that the directions given in the Specification are insufficient, but the Patent is for a principle of wide scope and there is no need for minute directions, because the process will work under all conditions. The invention has effected a revolution in the soap-making industry, and the Patent is a master Patent. The Specification describes a way of putting the principle into practice. *Lake's* Specification deals merely with the extraction of glycerine from fatty substances, and has no bearing on the invention here; nor has *Ramage's* Specification, which relates only to the drying of oils, without any hydrogenation. *Zürer's* process is merely for saturating fatty acids with chlorine, and then replacing the chlorine by hydrogen by heating under pressure with water and metals; there is no catalytic action. *Sabatier* and *Senderens* state generally the catalytic action of certain finely-divided metals in adding hydrogen to incomplete organic molecules, and then go on to deal with the substitution of hydrogen for oxygen. The Patentee's object is to keep the oxygen in the acids and oils, and to add hydrogen, and *Sabatier* would lead people away from that. The papers by *De Wilde* and *Reychler* and *Goldschmiedt* do not deal with catalytic processes at all. The Defendants allege non-utility, meaning that if the Patentee's directions are followed the result that he describes would not be obtained. Several of the allegations in paragraph 5 of the Particulars of Objections are mere general allegations that the Patentee's process will not work. Catalytic action was well known, and it was not necessary to give directions as to the mode of preparation of the catalysts. The claim is for the application of known catalytic methods to substances to which they had not been applied before — for obtaining an old product by a new method. The Patentee mentions nickel as a catalyst, as being the best metal for the purpose. A competent chemist would have no difficulty in finding what were the best temperatures and proportions.

Evidence was given in support of the Plaintiffs' case.

**Dr. A. Liebmann** stated that fats could not be vaporized. There

was nothing in literature as to anyone, prior to the date of the Patent, having acted with hydrogen as a catalyzer on a liquid; *Sabatier* had said the presence of the liquid was fatal and destroyed the catalyst. The liquid oils, after having been hardened and made into fats by the patented process, could be used for various purposes. In the case of the fish oils the disagreeable smell was destroyed, and cheap vegetable oils could be used for the manufacture of margarine, and oils could be rendered useful for soap-making or candle-making. Before 1903 it was known that it was impossible to obtain a vapour of a glyceride, and that a fatty acid could be distilled in super-heated steam, or under reduced pressure. Steam would probably oxidise the catalyst unless hydrogen was present, and it would be excluded from vaporisation. The witness had used a current of hydrogen for the vaporisation of fatty acids. He gave details of experiments he had successfully made in the application of the patented process.

Dr. F. W. *Passmore* stated, *inter alia*, that the great part of the invention was that it had shown the erroneous character of the old theory that anything that would tend to cover up the surface of the catalyst would destroy it, and had shown that it was possible to catalyse in fact.

Sir *James Dewar* also gave evidence.

*Walter K.C.* summed up the Plaintiffs' case. — *Moissan* and *Moureu* in 1896 dealt with the action on a mixture, of acetylene and hydrogen, of iron, nickel and cobalt prepared by reduction with hydrogen at as low a temperature as possible. They found that, when incandescence took place, part of the acetylene was polymerised, and part was split up. Their theory was that the porous state of the metal led to the condensation of the acetylene, and the evolution of heat, and that all bodies having that catalytic or pyrophoric structure must give an identical result. They referred, as to the precautions to be taken in obtaining the nickel, to the paper by *Moissan* in the "Annales de Chimie," 1880. Dr. *Passmore* said that he found instructions to obtain the hydrated oxide of nickel in a finely-divided state by precipitation from the nitrate, sulphate, or carbonate, and that the finely-divided nickel, obtained from that oxide by reduction at as low a temperature as possible, would be pyrophoric and decompose acetylene. *Sabatier* and *Senderens* continued *Moissan's* work, and, in their Papers on the action of nickel on ethylene, said that the reaction takes place with the catalytic nickel, with nickel reduced at a red heat, or even with nickel filings. Then they dealt with the conversion of ethylene into ethane by means of hydrogen and a catalytic agent. After that, they dealt with the hydrogenation of

acetylene in presence of nickel, and with the action of copper and of iron and cobalt on acetylene, and with the hydrogenation of ethylene in presence of various reduced metals, with the hydrogenation of benzene, and with the preparation of aniline from nitro-benzene and analogous nitro-bodies. The results show that it is impossible to say that the method that will act in some cases will act in others, or to see why the fatty acids do not wet or act upon the surface so as to inhibit the action of the catalyst. Nowhere throughout those Papers is there any work with other than pyrophoric bodies, except in the case of acetylene and ethylene. *Normann* continued the work. He referred to the literature telling how to prepare the catalysts, although he need not have done so, as the literature was part of the common stock of knowledge of chemists. He stated that the fatty acids, not their glycerides, may be treated in the vaporised condition. There is no mystery as to the method of converting them into vapours. It is a common operation to bubble hydrogen through a liquid, and get the vapour of the liquid mixed with hydrogen. And *Sabatier* described that method, and also the use of a capillary tube. Then came *Normann's* great discovery, that the fatty acids, and their glycerides, could be treated in the liquid condition. The explanation seems to be that the liquid does not wet the metal, just as oil will stick to metal and not to rock, and so float up the metal. As to the use of an oil-bath, that appliance is used when the temperature desired is from about 100° to 250°. All the experiments conducted at temperatures between these limits succeeded. No chemist would endeavour to obtain finely-divided nickel by first grinding the oxide. In some of the Defendants' experiments the oxide from which the nickel was obtained was ground; it ought to have been precipitated — grinding will not give the fineness required.

*Astbury* K.C. for the Defendants. — The precipitated oxide dries into a hard cake, that has to be ground. There is no evidence that *Normann's* process is useful. The solidification of oils in this country is only now coming into commercial use. An ordinary chemist might work on *Normann's* process for years, and obtain no useful result at all. The Specification is deficient as to any valuable directions, and is misleading. To obtain a useful result something must be done that is not even hinted at in the Specification or in *Sabatier's* papers. A catalyst that will work with one sample of some particular fatty acid or glyceride will not work with another sample. The whole matter is mysterious. *Sabatier* did not use the pyrophoric metal used by *Moissan*, and the Specification ought to have given directions on the point. The Specification may be construed as

saying that fats may be treated in the vaporised state, though it is sufficient for them to be treated in the liquid condition; and it is admitted that fats cannot be vaporised. The nickel used by the Defendants has been obtained by the ordinary process of reduction in hydrogen, and, if that is not sufficient, the Patent is invalid for insufficiency of the Specification. The Patentee says the temperature is immaterial, but no one has used a temperature below  $100^{\circ}$ , and some of *Sabatier's* processes take place in the cold. If *Normann* had tried besides nickel, iron, cobalt, and copper, he would have found out certain differences between their action and that of nickel, and in that case he ought to have disclosed the best method of carrying out the process. He says that water-gas may be used; that means commercial water-gas, which contains sulphuretted hydrogen and cannot be successfully used. The Claim is for applying catalysis to the fatty bodies by vaporising or by the liquid process. The Plaintiffs' witnesses state that if one makes reduced nickel by the processes described in the text-books one will fail, and Dr. *Liebmann* went so far as to say that one would probably fail if one bought nickel oxide in a shop and reduced it as told by *Sabatier*. The Plaintiffs say their case stands or falls on being able to confine their Patent to preparing the catalyst by the particular method described in *Sabatier's* and *Moissan's* papers. But *Moissan* describes the reduction of the hydrated sesquioxide of nickel obtained by the action of chlorine on the hydrate of nickel protoxide and neither *Sabatier* nor *Normann* suggests that it is necessary to use the oxide prepared in that way. The use of chlorine would "poison" the catalyst. The Plaintiffs say that the nickel, to be catalytic, must be pyrophoric, but pyrophoric nickel will not act in some cases. For some unexplained reason, it will harden one sample, say, of linseed oil, but not another sample. The action depends on the mode of preparation of the body from which the oxide is made, on something in the fatty body, and on the temperature. *Sabatier* is actually misleading, as he did not say that it is material how the oxide is made, and he did not say anything about the mode of preparing the bodies from which the oxide is obtained. Mr. *Balantyne* followed *Normann*, *Sabatier*, and *Moissan* and failed in every case. Then he had a suggestion from the Defendant *Testrup*, not given by the Plaintiffs' authorities, and in some cases he succeeded and in some he failed. He had found a similar result in repeating Dr. *Passmore's* experiments. Iron with acetylene is very pyrophoric, but iron as a catalyst for hydrogenation is practically useless; it will not act at all with liquids. The temperature at which the catalyst is prepared is immaterial except as to acetylene. *Sabatier* said that

the catalytic decomposition of ethylene takes place very well if the nickel has been reduced at a red heat, and in that case it is not pyrophoric. But the nickel is not so active as if it had been reduced at 300°, which is not *Moissan's* temperature. A chemist reading *Sabatier's* Papers would conclude that the density of the nickel is not increased by higher temperature, whether it is partly in the reduction or in the next process. *Sabatier* says the nickel must be freshly reduced; the Defendants have always freshly reduced theirs. He says that acetylene can be hydrogenised by sheet copper. There is not a single suggestion in *Sabatier's* Papers that one is to reduce from a hydrate, and from a body that itself has been prepared at a low temperature, and still less is there any suggestion that the temperature of reduction in any case should be *Moissan's* 240°, instead of 300°. The Specification is capable of being construed as meaning that the vapour process is applicable to the fats as well as to the fatty acids, that the expression "fatty acids," when used alone, stands both for the acids and their glycerides, the fats. The Patentee either knew, or did not know, that *Sabatier's* method would not act, that it was necessary to adopt *Moissan's* method of reduction from a higher oxide at a low temperature, and that the hydrate, instead of the oxide, must be used. If he knew any one of those three matters, which are essential to success, he has not mentioned them; if he did not know them, then he has not made an invention. And, even if the catalyst is prepared by the Plaintiffs' method, with certain of the fats and fatty bodies, no result is obtained. To infringe a master Patent by the use of an equivalent, the equivalent must be known at the date of the Patent to be an equivalent. In 1903 it was not known that, in acting catalytically on a liquid, it was equivalent to bubbling hydrogen through the liquid to take a fatty body and the metal and spray them into a chamber containing hydrogen under pressure, for it is admitted that no catalysis of a liquid was known at all, and none of the witnesses knew of any process, catalytic or other, in which the metal and body were sprayed together, or any liquid with metal in suspension in it was sprayed into a gas under pressure. That is an invention of *Testrup*, and will give results that the Patentee's process will not give. The Patentee says that temperatures are unimportant; *Sabatier* says they are most important; they vary greatly with each catalyst and body acted on; it is impossible to get any general law out of *Sabatier* at all. There is no evidence that the patented process has ever been worked.

Evidence was given in support of the Defendants' case.

*H. Ballantyne*, in answer to questions dealing with the point whether

a chemist would know that by obtaining nickel oxide through the hydroxide by precipitation, he would get the oxide in a more porous form, stated that a chemist could get the oxide in a bulky but finely-divided state, and that he would know that he would have a more finely-divided material than if he went to a higher temperature. The witness said that, as to specimens of nickel reduced from the oxide and nickel reduced from the carbonate, the latter would be more bulky, and more finely-divided, but would have a larger particle; the two specimens could both be sufficiently rapidly permeated by a gas, and the denser of the two would have better pyrophoric properties than the other, but pyrophoric activity was independent of catalytic activity; in the case of the hydrogenation of oil one is dealing with a liquid getting into a porous body. When the nickel oxide was reduced, nickel would, by the removal of the oxygen, be left in a cavernous condition, though there might be some contraction.

O. Hehner stated, that he had made a series of experiments—in which he used the purest oleic acid, and 2 per cent of the most active nickel reduced at  $360^{\circ}$  from purest nickel oxide for three hours. The rate of hydrogen flow was about 14 litres per hour, and the depth of the oil column 4 inches and the width  $1\frac{3}{4}$  inches. The temperatures throughout the respective experiments were  $90^{\circ}$ ,  $100^{\circ}$ ,  $120^{\circ}$ , and  $150^{\circ}$ . The original iodine absorption was 86.4 per cent. After 18 hours 10 minutes, it was reduced in experiment (3) to 85.1 and in (4) to 81.7, in (5) to 82.9, and in (6) to 61.8; and in the last experiment, after 57 hours 5 minutes, it was reduced to 45.5.

Dr. Julius Lewkowitsch stated, that before 1903 he had read *Sabatier's* earlier Papers and had tried to hydrogenate oleic acid, as vapour and as liquid, with nickel; but had failed. He had prepared the nickel by converting the sulphate into carbonate, converting that into oxide, and reducing the oxide at  $400^{\circ}$  or a little above. Then he had read the Specification, but had again failed. Later he had read *Sabatier's* Paper of 1905 and had succeeded after two years' work.

O. Hehner, recalled, stated, that, in preparing the nickel he used, he had made the green hydroxide, and treated it with chlorine, obtaining *Moissan's* sesquioxide.

Dr. A. Liebmann, recalled, stated in cross-examination, that he had made a number of further experiments. For one, he had bought nickel protoxide, reduced it at  $300^{\circ}$ – $320^{\circ}$  C., and used it for the hydrogenation of oleic acid and had succeeded.

Jenkins K.C. summed up the Defendants case.—The Patent is invalid, first, because the Patentee claims a process for converting unsaturated fatty acids into saturated compounds by a catalytic



method applied to the vapours of the fatty acids, which process is not useful; secondly, because he claims a process for converting unsaturated fatty acids, or their glycerides, into saturated compounds by a catalytic method applied to the vapours of the glycerides, which process is impossible; thirdly, because he claims the substitution of commercial gas mixtures for hydrogen in carrying out his processes, whereas the use of those gas mixtures renders the processes, if otherwise practicable, impracticable unless the mixtures are purified, and he gives no directions for their purification; fourthly, because he claims a catalytic method wherein metals other than nickel, and particularly iron, cobalt, copper, and platinum, are employed as the catalysers, which processes are impossible or impracticable; or, alternatively, the Specification is insufficient and misleading in that no sufficient directions are given as to the catalytic substance necessary to be employed to enable the invention to be carried out; and, fifthly, because the Specification is insufficient in that no sufficient directions are given to enable the invention to be performed so far as the same relates to the processes claimed for the conversion of unsaturated fatty acids or their glycerides in a liquid condition into saturated compounds. The first four reasons depend to a great extent upon construction, and do not involve much dispute as to facts. If any one of them is valid, it is possible that the Patent might be made good by amendment, but if the fifth reason — the broad attack — is valid then the Patent could not be made good by any amendment. If the Defendants succeed on any one of these points they are entitled to have the action dismissed. The first objection assumes, for the purpose of argument, that the Specification tells how the process can be carried out, but asserts that when carried out it is useless. As to the vapour process, the Patentee seemed not to know that the fats cannot be vaporized, as, in 1912, he applied for a Patent in the Transvaal and said in his Declaration that the glycerides might be exposed in a vaporised condition to the action of the hydrogen and catalyst. With regard to the use of commercial gas, which is the subject of a separate Claim, *Sabatier* removed the sulphuretted hydrogen that would be fatal to the process, but the Patentee gives the impression that purification is not necessary. The Defendants have shown that one cannot, by using iron, cobalt, copper or platinum as catalysts, bring about the hydrogenation. The Plaintiffs' witnesses say that they have effected the hydrogenation with iron, cobalt and copper in the vapour process; but the Defendants have shown that one cannot succeed with these metals or platinum in the liquid process. If the Patentee claims hydrogenation in the liquid process by a metal other than nickel,

the Patent is invalid. With regard to platinum black, the Plaintiffs have not shown that it will work with anything. They say that it is not material, that is a question of construction; and the Defendants say that the Claim includes finely-divided platinum. As to the general scope of the Specification, the expression "this catalytic method" means the use of the finely-divided metals to exercise a catalytic action with hydrogen as they did with oxygen. The Plaintiffs seemed to think that *Sabatier's Papers* were to be treated as if the Patentee had recited them, but that is a false construction. He did not recite them, but he recited prior knowledge so far as was known to him, and exhaustively, as he mentions platinum black, and makes it clear that he may include platinum sponge. Then he gives general directions that it is sufficient to expose the fat or fatty acid, in a liquid condition, to the action of hydrogen and the catalytic substance. That is the Patentee's claim. It is not narrowed by what follows. The Patentee has thrown his net very widely, and has taken a correspondingly heavy burden. He thought he had discovered a new principle, and had found that the supposed capriciousness of catalytic action did not exist. The Plaintiffs have been working on this subject for years, but they have not told the Court what they have been doing. It is difficult to avoid reading their subsequently-acquired knowledge into the knowledge of 1903. It may be said that the Patentee has prescribed, in a loose way, a range of temperature from 100° to 250° — the range of an ordinary oil-bath; but he has stated that the reaction will be obtained at 100° with every body treated. And, as he says that temperature is immaterial, he has not purported to give any range of temperature. The Plaintiffs have to choose between saying that the statement that temperature is immaterial is of general application, in which case the Patent is clearly bad, and saying that the direction merely refers to the instance given, of nickel, and that the statement means that having found a temperature at which the reaction is obtained, it is immaterial whether or not one goes higher. The instance, and the direction as to the oil-bath are not of the essence of the invention. It has been proved that the temperature and the proportions are vital. As to the water-gas, if one purifies it, one does something that makes the hydrogen operative, and so the process comes within Claim 1. If the words "temperature is immaterial" are of general application to the Specification, they are misleading and invalidate the Patent; if they refer only to the specific instance then the Specification is insufficient as to the general process. The differences of opinion between the experts have been narrowed down to the mode of preparation of the catalyst — the nickel. Mr. *Hehner*

used temperatures of about  $300^{\circ}$  for the reduction of the oxide, and sometimes went to  $340^{\circ}$ ; Dr. *Liebmann* went as high as  $360^{\circ}$  in one case. The question is further narrowed down to the preparation of the oxide. The process can be carried out with finely-divided metal obtained from any oxide, but only with certain bodies, and with certain precautions. *Moissan's* Papers have no bearing on the matter. His Paper of 1880 was simply directed to the investigation of the allotropy of certain oxides. The experiments of the Plaintiffs' witnesses had, in order to succeed, to be conducted with special stirring apparatus and a strong current of hydrogen, precautions that are not indicated by the Patentee. The failure of Dr. *Lewkowitzsch* to obtain *Normann's* results, although following his Specification carefully, shows that the Specification is insufficient. The Patentee assumed that the catalyst that would act with the gases would act with the liquids, and it turned out that it would not. As to infringement, the Defendants' method is an improvement on the Patentee's, and if his claim is limited to his precise description, it is not an equivalent.

Sir A. *Cripps* K.C. replied. — As to the knowledge at the date of the Patent, the references to *Sabatier* imply a reference to *Moissan*, and *Sabatier* says that the best method is to prepare the catalyst in the way described by *Moissan*, that is, in order to get a porous oxide, hydrate should be used. The Plaintiffs' witnesses went through the sesquioxide and the hydrate to the protoxide, and showed that the process worked best in that way. They tried further experiments with oxides made from the carbonate, sulphate, and nitrate, and succeeded. The invention is of enormous value; it is said to be worth a quarter of a million a year; and there can be no question as to utility, or as to the sufficiency of the statement of the invention. The only question is as to the sufficiency of the directions. The stirrer and the strong current of hydrogen used by the Plaintiffs' witnesses were expedients such as would naturally be adopted by a chemist wishing to get contact between the reagents. Supposing the invention to be the hydrogenation of unsaturated fatty acids, and oils so as to saturate them, and the Patentee gives one example that works, that is sufficient. Possible complications with different catalysts have nothing to do with the matter. With regard to the presence of sulphuretted hydrogen in water-gas or illuminating gas, a chemist would know that sulphur is a "poison" to the catalyst and would remove it from the water-gas, and it is not found in modern illuminating gas. The direction that the catalyst is to be finely divided is sufficient to indicate that it is to be as finely divided as possible. The use in the

Claim of the expression "adapted to act as a catalyst" has been objected to, but such a description is properly employed in a claim for a wide principle. The further experiments of Dr. *Liebmann* and Dr. *Passmore* were conducted in accordance with the directions given in the Specification. They started with a fine nickel powder obtained by reduction in a current of hydrogen, added to it oleic acid, as pure as possible, heated it over an oil bath and passed a strong current of hydrogen through it, so as to keep the metal in a state of suspension. They succeeded, and the only objection made is that they added stirring, but that is an expedient that would naturally and properly be adopted.

Neville J. — The Specification in the present case is short and artificial. The Patentee discloses, I think, clearly enough what he claims to have discovered. It was, in the first instance, that the saturation by hydrogen or hydrogenation of unsaturated fatty acids and their glycerides, fats and oils, could be attained by catalysis. In introducing his discovery, he refers to the fact that it had already been disclosed that, in certain cases, catalytic action with hydrogen had been brought about by the presence of finely-divided platinum, and further that *Sabatier* and *Senderens* had extended discovery in this direction by showing that other finely-divided metals, namely, iron, cobalt, copper, and especially nickel, might take the place of platinum. He tells us that *Sabatier* — I will use this name as including *Senderens* — obtained saturated hydrocarbons from unsaturated hydrocarbons (partly with simultaneous condensation, which I take to mean what he calls later secondary reactions), namely, acetylene, ethylene, or benzene, by causing their vapours mixed with hydrogen gas to pass over one of the said metals. Reading the Specification as a whole, I think he then proceeds to tell us that his discovery is that it is easy by "this catalytic method" — which means, I think, hydrogenation by catalysis — to hydrogenise all kinds of unsaturated fatty acids and their glycerides, that is to say, fats and oils. I may say, in passing, that the glyceride is merely the fatty acid with the addition of glycerine, and the fats and oils, thus composed, differ from the fatty acids in this respect, that while fatty acids may, under certain conditions be vaporised, fats and oils cannot. How to vaporise a fatty acid the Specification does not tell us, but *Normann* says that hydrogenation of the unsaturated fatty acid may be obtained by causing it in vapour with hydrogen to pass over the catalytic metal. This vaporisation, however, he declares to be unnecessary, since it is sufficient to expose the fat or fatty acid — that is to say, any unsaturated fatty acid or its glyceride — in a liquid condition to the action of hydrogen and the

catalytic substance. The evidence shows the advantage of treating the fats and fatty acids in the liquid state without vaporisation to be very great, and I think *Normann* did not intend to indicate vaporisation as part of his process, but to point out that you could obtain hydrogenation by a far simpler method. To dismiss this point at the outset, I do not think, upon any construction of the Specification, that the difficulty of vaporisation, even if it were as great as the Defendants suggest, would avoid the Patent. If the Specification is sufficient in other respects, what *Normann* here says is true, and, even if the process by vaporisation is of no commercial value, the liquid process is, and I think the Patent would stand. Having told us that treatment in the liquid state suffices, *Normann* discloses an instance in which he alleges that pure oleic acid may be completely converted into stearic acid, that is, a non-saturated fatty acid into a saturated fatty acid. I think, if he has described a process by which this may be done, and if that process is effective with all fats and oils and all other fatty acids in combination with any "finely-divided metal adapted to act as a catalyser" (including platinum, iron, cobalt, copper, and nickel), the Specification would be sufficient. Indeed, I should be inclined to hold that, if the invention was substantially co-extensive with the Claim, proof that some fatty acid or oil could not be successfully treated by one or more of the catalysers mentioned was immaterial, so long as the exception was of no commercial importance.

There are minor points upon the construction of the Specification raised, such as the possibility of using commercial gas mixtures as a substitute for hydrogen, but I will, in the first instance, examine the question of whether the process which *Normann* describes will effect the result which he claims for it, and I will here say that, if by his process a substantial saturation is effected, sufficient for technical purposes, I should not consider its failure to ensure complete saturation fatal, notwithstanding that he has stated that the oleic acid may be completely converted into stearic acid; nor should I think it fatal if some secondary reaction took place, notwithstanding his declaration to the contrary, so long as such reactions did not substantially interfere with the utility of the process.

In my judgment, the right of a Patentee to his monopoly is essentially a matter of substance, and the question to be decided a broad one, namely, whether he has in substance given the consideration which the grant of the Patent requires.

Now let us turn to *Normann's* Specification and see what are the conditions to be fulfilled to obtain the result which he indicates. First of all, nickel powder obtained by reduction in a current of hydrogen is

to be procured. There is no special meaning, I think, to be attached to the word "powder," except that the product is to be in a fine state of division; but the evidence shows that, if metallic nickel is to be obtained by reduction, it must be obtained by reduction of the oxide; so we take finely-divided nickel obtained by reduction of nickel oxide in hydrogen and add it to chemically pure oleic acid. For pure oleic acid, we may substitute any commercial fatty acid, or fat, so far as the method is concerned; though, of course, if we do, we cannot expect complete conversion of the whole compound, inasmuch as impurities may be expected. Then the oleic acid is to be heated over an oil-bath. No temperature is mentioned. The ordinary temperatures for which oil-baths are used are variously stated as extending from 50° or 100° to 250° C., but, inasmuch as the inventor tells us immediately after that the quantity of nickel added and the temperature are immaterial and will only affect the duration of the process, I think it is impossible to construe the Specification as giving any direction as to the temperature to be employed, unless, perhaps, one may say that, as heating is directed, it should be something above room temperature — how much, I think, one does not learn. A strong current of hydrogen is to be passed through the mixture, and I think it is common ground that the current should be strong enough to keep the metallic nickel suspended in the liquid in order to give the opportunity of contact between the surface of the nickel and the molecules of the other bodies.

Before proceeding further, I will put in untechnical language what I understand from the evidence to be conveyed by the word "catalysis." It appears that in the presence of, or in contact with, certain metals, chemical bodies undergo changes which do not otherwise take place. The reactions induced by the presence of the catalyst may involve merely the splitting up of a single chemical body, of which the decomposition of acetylene in the presence of finely-divided nickel is an instance, or the combination of two chemical bodies which, but for contact with the catalyst, would have retained their composition unchanged, although in contact with one another. The hydrogenation of a fatty acid where hydrogen and the fatty acid are brought into contact in the presence of a suitable catalyst is an instance of the latter kind of reactions, and that which forms the subject-matter of the present invention.

To return to the Specification, the experiments made by Mr. *Ballantyne* and Mr. *Hehner* show that you may take finely-divided nickel, or nickel powder, obtained by reduction from the oxide in a current of hydrogen, and add it to pure oleic acid or any other fatty acid, warm the mixture, and pass through it a strong current of hydro-

gen, without obtaining the catalytic reaction indicated by the Patentee at all. That, by preparing your nickel powder in a special way and raising the temperature to a certain degree, you may obtain the result required, although the reaction appears to be very capricious, is shown by the experiments of Dr. *Liebmann* and Dr. *Passmore* and admitted by Mr. *Ballantyne*. The Plaintiffs' contention is that the success of Dr. *Liebmann* and Dr. *Passmore* is conclusive to establish the validity of the Patent, for it is said that these gentlemen did no more than the Specification directed. They say that it was known in 1903 that catalysis was a surface or contact action, and that, for the purpose of obtaining contact, the finer the division the better the chance, and that it was known that, for the purpose of catalysis, the oxide should be reduced to the metal at the lowest possible temperature, or at about 300° C. Therefore, they say that any competent chemist upon reading the Specification would, as of course, take nickel oxide as finely-divided as possible, and reduce it in hydrogen at a temperature of from 300° to 350°.

I pause here to state certain conclusions at which I have arrived upon the evidence. It appears that the fineness of division of the nickel — by which is meant the minuteness of the pieces composing the substance, depends — not upon the temperature (within the ranges of temperature which are dealt with here) at which the oxide is reduced to the metal, but upon the physical state of the oxide with regard to minuteness of division at the time when the reduction commences, the number of pieces of metal after the reduction being substantially the same as the number of pieces in the oxide. Therefore, the temperature at which the reduction takes place is in this connection immaterial. The activity of a catalyst does not, however, I think, depend solely upon minuteness of division, but upon the porosity of the pieces of metal composing the powder. In the course of reduction, when the oxide gives up its oxygen, the metal left behind is in a porous, or what has been described as a cavernous condition, the result being that, inasmuch as the fatty substance may be able to penetrate into the cavities, a greater surface is afforded for contact than if it were in a denser or more solid condition. This distinction has, I think, not been sufficiently regarded in some parts of the evidence, the words "finely-divided" having been sometimes used to denote porosity, rather than the smallness of the pieces into which the metal is divided. Mr. *Ballantyne*, explaining the different qualities required for pyrophoric purposes and catalytic purposes, speaks of metal in larger particles or grains being more finely-divided than metal in smaller particles or grains. I do not think that, in fact, the words

"finely-divided" have a meaning in chemistry different from that which they bear in English. The effect of heating is to cause the porous metal to contract and become denser; hence the desirability of reducing the oxide at a low temperature; and I think to-day it would be common ground that the most promising catalyst for hydrogenation would be a suitable metal in the highest state both of fine division and porosity. At the same time, it must be remembered that this so-called catalysis remains unexplained. All that is known about it is, that it happens, and no one can safely predict what will happen in any case not already tested by experiment. Nothing seemed more unlikely before *Normann's* discovery than that this catalytic method should be available for the saturation of fats and oils.

Papers by *Moissan* and *Sabatier* are relied upon by the Plaintiffs in two ways: first, because *Sabatier* is referred to in the Specification, and *Moissan* is referred to by *Sabatier*, and it is said that this is an express reference by the Patentee adding to the information given by the Specification all the information to be gleaned from these Papers, and in them, it is said, are to be found directions how to prepare your catalysts for *Normann's* invention; and, secondly, it is said that, at all events, what was contained in them was public knowledge, and the hypothetical competent chemist was bound to supplement the Specification with the knowledge acquired from *Sabatier*.

The first contention is, in my judgment, untenable. It may perhaps be permissible for a Patentee to say in his Specification: — "For the purpose of carrying my invention into effect, I refer you to such "and such a publication in which you will find all necessary directions." I doubt if this would fulfil his obligations to the public, but, at all events, on turning to the publication indicated, you must find in clear and precise terms the very process which he claims, or one which, without further experiment, can be applied for the carrying into effect of his invention. To turn the hypothetical chemist loose into the labyrinth of long chemical papers dealing with a variety of subjects more or less connected with the matter in hand, and tell him to search for himself and adopt for the purposes of the invention what he deems applicable, would be to fall altogether short of his duty as patentee. On the question of common knowledge, I think there must be shown something more than the fact that there has been recently published information which, though not directed to the matter in hand, ought, if properly understood and digested, to have led the inquirer to adopt certain methods and precautions in carrying out the invention with regard to which the Specification is silent. But further, if every line of *Moissan* and *Sabatier* were read, I do not



think it would lead the inquirer to suppose that any particular method of preparing the oxide for the purposes of *Normann's* process was necessary, nor indeed, as the experiments show, was it. *Moissan's* Paper is a description of an isolated demonstration of the reduction of a sesquioxide of nickel prepared in a particular way through various transformations down to metallic nickel, and is referred to by *Sabatier* in a Paper but remotely bearing upon *Normann's* invention. It is true that *Moissan* declares that the resulting metallic nickel will be pyrophoric, but it appears to me that there is no direct connection between a metal being pyrophoric (that is, being in a state in which it will oxidise in ordinary temperature at a white heat) and being a catalyst which can be relied upon to realise successfully *Normann's* invention. Indeed, the fact that some of the catalysts used by Mr. *Ballantyne* and Mr. *Hegner* in unsuccessful experiments were pyrophoric, seems conclusive on this point. I think, therefore, the question of how to prepare a finely-divided metal so that it may be pyrophoric is not relevant to the present case.

I come to the conclusion, upon the evidence, that *Normann's* process will not produce the result he claims for it unless the fine nickel powder is obtained in a special manner not indicated by the Specification, or unless a very strong current of hydrogen is used, and mechanical stirring or some other special device is resorted to. The possible effect of violent agitation in keeping the surface of the catalyst free from the poison of the oil is pointed out by Mr. *Ballantyne*. No hint of such a necessity is to be found in the Specification, and I think the hypothetical chemist was entitled to suppose that the process described in the Specification was sufficient to effect its purpose, and, having applied that process and failed to produce the result, was entitled to consider himself misinformed, without resorting to experiment to see in what manner the directions failed. The discovery was entirely new and contrary to anticipation, and the process described by *Normann*, for all that was generally known on the subject, might very well have been sufficient. There was no reason to presume any necessity to add to the directions, which he gave, anything from the stock of common knowledge. What appears to me very strong confirmation of the insufficiency of the Specification is to be found in the evidence of Dr. *Lewkowitsch*, a great authority on the subject. Dr. *Lewkowitsch* had endeavoured himself to obtain the saturation of oleic acid by the use of nickel as a catalyst and had failed. He afterwards became acquainted with *Normann's* Specification, and tried a further series of experiments with no greater success. He had obtained his catalyst from a solution of sulphate of nickel.

He afterwards read some further Papers by *Sabatier*, published in 1905, recommending amongst other things the use of nitrate in place of sulphate of nickel, and pointing out that nickel lost its catalytic properties if exposed to too high a temperature. With these hints, Dr. *Lewkowitsch* recommenced his experiments, and after several years succeeded in solving the problem. It is said for the Plaintiffs, and truly said, that sulphur was known to be what is called a poison to a catalyst and that therefore sulphate of nickel ought not to have been employed, but the precipitate was properly washed, and there was, in 1903, no reason to suppose, if this was done, that sulphur to an injurious extent would remain. Moreover, no warning is given in *Normann's* Specification against the use of sulphate of nickel, or as to the temperature to be employed in reduction. The evidence in this case shows that a catalyst prepared from the sulphate may be successful, and also that nickel may be heated to a red heat without destroying its catalytic properties. Certain passages in subsequent publications of Dr. *Lewkowitsch* have been referred to as discounting the evidence given by him in this action. It seems to me that they do not diminish the weight of his testimony. Here was a chemist, having special acquaintance with the subject, who tried a method of saturating oleic acid, identical with that described by *Normann*, and failed, studied *Normann's* Specification and, after repeated experiments, again failed, and, after receiving what he says was a clue from a publication by *Sabatier* in 1905, succeeds only then after experiments extending over several years. So that we find a chemist of exceptional qualifications, deeply interested in the subject, failing for years, after repeated experiments, and careful study of *Normann's* Specification, to achieve what I am asked to believe any competent chemist could, in 1903, have achieved by following *Normann's* directions. without any experiment at all.

In this connection I cannot but remind myself that, though the Patent was taken out in 1903 and purported to reveal a process of immense commercial value, no evidence has been called to show that anyone succeeded in taking advantage of the discovery for a considerable number of years after its publication; that the only evidence of sufficiency is the evidence of eminent chemists who essay to prove by experiments in 1912 that the directions contained in the Specification were in 1903 sufficient to ensure success.

I come to the conclusion that the directions in *Normann's* Specification were insufficient; and I infer, both from the evidence before me, and the lack of evidence, that, great as the discovery that unsaturated fatty acids and their glycerides could be hydrogenated by the catalytic

method undoubtedly was, no practical means of taking advantage of the discovery were disclosed until after further experiment subsequent to the date of the Patent.

It has been repeatedly urged that, catalysis depending upon contact, the difference between success or failure is simply a question of obtaining or failing to obtain contact. In my opinion, the evidence fails to establish this in any material sense. There is nothing to show that the directions of *Normann* do not suffice to get contact. Catalysis remains a mystery to-day, and in 1903 nothing whatever was known as to the means necessary to obtain successful contact in the catalytic hydrogenation of oleic acid, or any other fatty acid or glyceride, except what was disclosed by *Normann* himself. According to Mr. *Ballantyne's* evidence, a catalyst which succeeded in getting "contact" in this sense with acetylene after *Sabatier*, failed with *Normann's* process. To say that a direction to pass a strong current of hydrogen through a mixture of fine nickel powder and oleic acid, in order to expose the acid to the action of hydrogen and the catalytic substance, connotes the resort to every device known to science for making the exposure as complete or as frequent as possible, seems to me extravagant.

I therefore come to a conclusion adverse to the Plaintiffs' contention upon their own case; but I do not concur in the construction of the Specification put forward on their behalf. It has been contended that this is a Patent for a principle, and that if the Patentee shows one way of carrying it out he is entitled to claim for all ways. If *Normann* had invented the hydrogenation of oleic acid by help of a nickel catalyst, and had given sufficient information in the instance stated to ensure success, then I think he could rightly claim all other ways of arriving at the result; but here he claims to have invented a method of obtaining hydrogenation of all unsaturated fatty acids and their glycerides, and if his method fails in any one case I think his Patent would be bad. Moreover, he claims to be able to secure the result by the use of finely-divided platinum, iron, cobalt and copper as well as nickel, and if the use of any one of these catalysts is fatal to his process I think his Patent is bad.

There are other matters arising in the action which, having regard to the view already expressed, are not necessary for the decision of the case; but I may say that I think that the evidence shows that the temperature at which hydrogenation is attempted is material, not only with regard to time occupied in obtaining the desired reaction, but for obtaining such reaction at all. It may be that one element of success is the mixture of oxide of nickel with the metal. Dr. *Liebmann's* experiments, were with reduction at a low temperature, 300° to 320°

for a short period, one hour, while Mr. *Hehner* in the experiments referred to reduced at 360° for three hours. I think the evidence shows that the temperature and time employed by Dr. *Liebmann* cannot be relied upon to obtain complete reduction. It will be observed that both Dr. *Liebmann* and Dr. *Passmore*, when seeking to demonstrate that catalysts prepared in a manner similar to that adopted by the Defendants' witnesses could be used, not only in all cases resorted to stirring, but used a much larger current of hydrogen than that used in previous experiments. Having heard the evidence upon the point, I will add that, could *Normann's* Patent have stood, in my judgment, the Defendants would have infringed it.

In the result, I am of opinion that the Plaintiffs' action fails and must be dismissed with costs.\*

As the statement has repeatedly been made that the British patent to *Normann*, for hardening fats, had been declared void because it claimed a process which had become public property, the Oelwerke Germania \* have taken occasion to contradict this assertion, claiming that the British court held the patent void solely because of an insufficient description of the process; thus merely on account of a purely formal defect in a peculiar requirement of the British patent law. This concern observes that there are no requirements in the German patent law such as contained in the British patent law, and, that in no wise did the British court hold the process to be public property; on the contrary, it stated emphatically that if this defect in the specification had not been present, judgment would have been given against the defendant for infringement of the patent. The formal defect at fault has, in the meantime, been removed by a process peculiar to the British law. The further statement is made that the British statute places more extensive requirements on the patent specifications than does the German statute, even in such matters as are incidental to the specific nature of the invention concerned. In case of insufficient observance of these requirements on the part of the applicant for patent, the patent may subsequently be invalidated on motion; on the other hand, a patent thus declared void may be re-established by removing the defect in the specification or by supplementing the specification.

\* Seifen. Ztg., 1914, 1260.

## APPENDIX B

### EDIBLE HYDROGENATED FATS. PATENT LITIGATION. CRISCO AND KREAM-KRISP

Litigation between the Procter & Gamble Company and the Berlin Mills Company involving the status of a patent owned by the former concern has brought forth many matters of general or historical interest in the field of oil hardening and the endeavor has been made to include here extracts from the briefs of the opposing parties, sufficient in extent to embrace what appear to be the more important data and discussion. Lack of space forbids the publication of the record in full and for complete details the reader is referred to the Court records.\*

The author is indebted to Mr. Alfred M. Allen † for a copy of the brief for plaintiff and to Mr. John C. Pennie ‡ for a copy of defendant's record, for which thanks are gratefully acknowledged.

#### UNITED STATES DISTRICT COURT, SOUTHERN DISTRICT OF NEW YORK.

THE PROCTER & GAMBLE COMPANY, <i>Plaintiff,</i>  <i>vs.</i>  BERLIN MILLS COMPANY, <i>Defendant.</i>	In Equity. No. 13-100.
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#### BRIEF FOR PLAINTIFF.

*Before JUDGE AUGUSTUS N. HAND.*

---

KERR, PAGE, COOPER & HAYWARD,  
*Solicitors for Plaintiff.*

LIVINGSTON GIFFORD,  
ALFRED M. ALLEN,  
THOMAS B. KERR,  
*Of Counsel.*

\* Citations to court decisions and the record have been largely omitted.

† Of firm of Allen & Allen, Cincinnati, Ohio.

‡ Of firm of Pennie, Davis, Marvin & Edmonds, New York City.

This suit is for infringement of patent No. 1,135,351, granted to the plaintiff as assignee of John J. Burchenal on April 13th, 1915, for a Food Product. The bill was filed on December 16th, 1915, the answer filed on January 14th, 1916, and an amendment to the answer was filed on September 22d, 1916. The answer set up a large number of prior publications and patents to show anticipation and the prior state of the art bearing on the subject. Bill of particulars were granted both parties and the issues narrowed to a certain definite number of prior patents and publications and to the first and second claims of the patent in suit. Prior to the trial the defendant took a large number of depositions *de bene esse* which have been printed for the use of the court in a book of 410 pages entitled "Defendant's Exhibit, Depositions *de bene esse*," which depositions were offered and admitted in evidence at the time of the trial. The trial began on March 21st and was completed March 29th, at which time the argument and filing of briefs was set for April 28th.

The defenses set up were anticipation, prior invention by one Kayser, lack of invention, limitations by Patent Office proceedings, insufficiency of specification and non-infringement.

\* \* \*

#### THE PATENT IN SUIT

In making the product, the patent says:

In manufacturing this product cottonseed oil or other vegetable oil is caused to chemically absorb a limited amount of hydrogen by reacting on the oil with hydrogen in the presence of a catalyzing agent and at an elevated temperature.

\* \* \*

The only claims in issue are claims 1 and 2, which are as follows:

1. A homogeneous lard-like food product consisting of an incompletely hydrogenized vegetable oil.
2. A homogeneous lard-like food product consisting of incompletely hydrogenized cottonseed oil.

\* \* \*

The great benefit of the invention is not mentioned in the patent, but really constitutes the basis for an award in favor of the patentee, namely, that it was the creation of a new class of food products of superior quality, free from the objections existing against animal products, and was the foundation of a now great industry known as the Hydrogenated Food Product Industry, which has conferred an enormous benefit upon the public and entitled the inventor to be enrolled high in the ranks of its benefactors.

\* \* \*

In both the processes of manufacturing Crisco and Cream-Krisp "the amount of hydrogen absorbed is carefully regulated and limited" by the operator, so that Crisco is given a melting point of 34 to 36 C., and the sample of Cream-Krisp in evidence was given a melting point of 35.7; the melting point given in the patent being from 33 to 40. By stopping the hydrogenizing when the melting point has reached any of these degrees, or even a degree slightly in excess, the "product which

cools to a white or yellowish semi-solid" is obtained, which is specified in claims 1 and 2.

It is thus seen that the gist of the novelty of the process, namely, that "the operation is stopped when the oil has been converted into a product which cools to a white or yellowish semi-solid" is followed by defendant in making Kream-Krisp, the same as by the plaintiff in making Crisco, and that the melting-point test by which defendant secured this semi-solid result was, in the case of the Kream-Krisp in evidence, with the range of Crisco melting point, and also the patent in suit melting point.

Since all three melting points are within the same narrow range from 33 to 40, it is inevitable that all three are semi-solid, or lard-like, at ordinary temperature, and the evidence shows conclusively, that that is what the average cook wants.

Moreover, by an inspection of the specimens of Crisco and Kream-Krisp in evidence the court can see for itself that they are lard-like. Certainly no expert is needed for that.

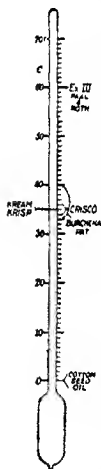
\* \* \*

In the infringing manufacture defendant uses the thermometer only to keep its product at the desired semi-solid or lard-like consistency. By the aid of the thermometer the hydrogenizing is "carefully regulated and limited." If, therefore, no test but the thermometer is used in carrying on the infringement, why should any other test be applied by the court in deciding the question of infringement? And, if any chart is desired, why should any chart be used more than the thermometer scale?

On this page we have produced a Centigrade thermometer scale from zero up to 70 degrees, and noted thereon the melting points of various products.

It will be seen that on this scale the hard approximately saturated cotton-seed oils (60°) and Paal & Roth (59°-60°) range themselves at one end and liquid cottonseed oil stands at the other end, while approximately midway range the semi-solid or lard-like in a bunch, between 33 and 40 degrees. Of course a slight variation of a degree or two above 40 would make no substantial difference.

\* \* \*



It appears from the testimony that Burchenal was the first one in whose mind the thought ever arose to associate a hydrogenized body with food. He was the first one that ever even asked the question whether it might be a food, and he was answered by Kayser in the negative. He was the one that followed up that question by the experiments necessary to determine the answer in the affirmative; and having embodied that answer in a successful food compound, he was the first to make the additional conception and discovery of the possibility that it might be a successful food product in still a second form, to wit, the partially hydrogenized form. He it was that made the necessary experiments to answer the question whether this idea was possible or not; and the generic conception had been made and worked out in the form of the compound in the spring of 1908, a year and a half before the specific conception

was made or worked out in the fall of 1909 in the form of the partially hydrogenized product, which is the subject of claims 1 and 2 in suit.

Burchenal's conception had its rise under the following circumstances:

Soap makers in England, the Crossfields in particular, had introduced hydrogenized cotton seed oil into the soap making industry.

The plaintiff was engaged in the manufacture of soap in this country, and in the fall of 1907 it received a letter from E. C. Kayser, dated Cheshire, England, October 18th, 1917, as follows:

"Dear Sirs:

"In a few weeks' time I shall be en route to the States, when I propose introducing a new process of the greatest possible importance to soap manufacturers.

"I have manipulated this process for the last three years and am the only person thoroughly acquainted therewith.

"Kindly inform me by the earliest mail if you wish me to call upon you in the first instance and if in that case you are agreeable to refund railway fares from New York or other port to your city.

"Yours faithfully,

"E. C. KAYSER."

In response to this letter plaintiff wrote under date of October 28th, 1907, inviting Kayser to come to Cincinnati, Def. Dep., p. 208, bringing with him samples of hydrogenated material being used by the Crossfields in making soap.

These samples were shown by Kayser to Burchenal, who describes them "hard almost white in appearance," Def. Dep., Ans. 40, "a very hard material, had a very high melting point, had an unpleasant taste" Def. Rep., Ans. 276; "very hard, a good deal the appearance of a piece of porcelain or china."

Procter & Gamble made a preliminary agreement with Kayser, dated December 5, 1907, to make what the agreement referred to as "hardened" material. Thereupon they erected an apparatus for Kayser and he proceeded with his experiments. His sole effort was to make a substantially saturated material. Burchenal testified:

"The sole effort was toward making a saturated material. That was indicated by its hardness" Def. Dep., Ans. 158. "The effort was to make a saturated material and wherever we didn't get that, we didn't look upon it as a successful operation," Def. Dep., Ans. 182. "Hard material—that was where our effort was at that time." Def. Dep., Ans. 164. "There was really no object and no sense in taking them" (samples to ascertain the progress of the operation.) "We were trying to saturate the material and that was indicated by the absorption of hydrogen. I can't say we did not take samples, but in the ordinary conduct of things there was no occasion to take samples."

Kayser's report of January, '08, said:

"Completion of saturation is indicated by comparison of volume of gas in and out of machine. When saturation is practically complete, the gas passes through without any apparent reduction in volume."

The hydrogenized oil cannot be used as soap without chemical change. It is



treated chemically with an alkali, such as potash or soda, or saponified, and it is this saponification of the hydrogenized body which is soap.

The first time that anybody seems to have associated any hydrogenized body with food was when Burchenal asked Kayser the question in October or November, 1907:

"I asked him if he thought it would do for edibles, and he said he thought not."

It is not difficult to realize why it had never been associated with the food art before, because as pointed out by Burchenal, "it did not appear to be edible; it was a very hard material, had a very high melting point, had an unpleasant taste."

McCaw in reference to a sample of this Kayser material submitted to him by Mr. Procter, says:

I immediately tasted it, examined its texture, and he asked me if I thought a lard substitute could be made from it, that is, if it would take the place of oleo stearin. I replied that it would not, giving as my reasons that the flavor, structure and material, and its hardness, were all unfit for that purpose.

It should be remembered too that it was already associated with the soap making art by the Crossfields, and that to be used as soap it first had to be chemically changed or saponified; all of which was antagonistic to any idea of its being used without saponification, and particularly for food. Moreover to any one familiar with the complexities of cotton seed oil and its hydrogenization, the presumption was that it would contain ingredients entirely incompatible with food requirements, and possibly even poisonous.

Following his own idea, which does not seem to have been shared by any one else, that it might constitute a food, Burchenal followed the matter up. He says:

"As soon as I saw the material that he (Kayser) brought there, I made up my mind that I would endeavor to ascertain if it was edible. I went into the thing, I examined the material; we worked on that."

Burchenal also proceeded to mix the hard, hydrogenized product with cotton seed oil so as to reduce it from its inedible hardness down to an edible semi-hardness. He had considerable difficulty in doing this, and sent the hardened material down to the McCaw Company in Macon, Georgia, about May, 1908, because of their having proper machinery for mixing. At that time the idea of the availability of a partially hydrogenized substance had not entered his mind. The sole idea up to that time was to completely hydrogenize and then reduce the hardness by mixing with cotton seed oil, and Burchenal appears to have entertained this idea as the sole means of attaining a food product until about a year and a half after he had had his first mixture made, or until the autumn of 1909. Burchenal testifies:

Well, how long after that (after spring of 1908) was it that you first produced a food product consisting of an incompletely hydrogenized vegetable oil? A. Well, I think our first report on that is some time in 1909. I would like to qualify that, however, so as to show that that material was not produced in a commercial way at that time, and was experimental.

Mr. Burchenal says:

I think I am safe in saying that the date on which that material was first produced in any appreciable quantities, was after April 26, 1910, and in all probability prior to July 1, 1910. \* \* \* In an experimental way, I should say about October or November, 1909.

Morrison (defendant's *de bene* depositions, p. 316,) testifies:

Q. 21. When did you first have the semi-solid hydrogenated cotton-seed oils sent to you for examination as to their physical characteristics?

A. Some time in 1909 was when I first came in contact with it.

Thus we have brought the history of the rise and progress of Burchenal's invention from the conception of a food possibility, through the various stages, down to the making of the product which is the subject of claims 1 and 2 in suit, covering a period of upwards of two years from the fall of 1907 until the fall of 1909, or the spring of 1910. It was first put on the market in April, 1911. Taylor, Ans. 11 and the sales thereafter were for 2,600,000 lbs.; 1912, 14,500,000; 1913, 23,800,900; 1914, 40,000,000; 1915, 47,700,000 and 1916, 60,500,000, or about 190,000,000 lbs. At the price ruling in 1916, this would make a value of over \$34,000,000.

The various stages of Burchenal's progress may be summarized as follows:

1. Fall of 1907. Conceived possibility that the hydrogenated substance might be utilized in the food product art, notwithstanding its intrinsic evidences to the contrary.

2. Winter of 1907-8. Discovered the correctness of his conception by investigation of the hard, hydrogenized product.

3. Spring of 1908. Invented a household form embodying said conception and discovery (i.e., the mixture or compound which is the subject of his patent 1,135,935).

4. From spring of 1908 to fall of 1909. Perfected the compound and introduced it commercially as "Flake White."

5. Fall of 1909. Conceived of the possibility of the improved form (i.e., the partially hydrogenized form which is the subject of claims 1 and 2 in suit.)

6. Fall of 1909. Invented Crisco as the embodiment of said last conception.

7. 1909 and 1911. Perfected Crisco and introduced it commercially.

8. 1911 to 1916. Sales of Crisco amounted to over 189,200,000 pounds, representing a market value of over \$34,000,000.

\* \* \*

It is well to pause for a moment to consider how beneficent are these household products.

From the physiological standpoint they are free from all detrimental ingredients or properties. Being all vegetable they are so free from the suspicion of microbes of animal origin that they are immune from the government inspection at the factory of animal food products. Crisco in particular is free from indigestible components.

From the household standpoint Crisco requires a minimum of skill or exertion to distribute it throughout the dough, and it remains so distributed throughout the cooking operation. It is less susceptible to oxidation and consequent ran-

idity than the liquid oil. It is less susceptible to smoking or burning because it can be heated to a higher temperature without doing so. Being lard-like, the ordinary cooking recipes requiring lard are satisfied by it, and it can be scooped out of its container and measured conveniently and accurately as is lard.

Added to all the above advantages is the fact that the introduction by Burchenal of hydrogenized substances into the food product art has enormously enlarged the resources of that art and prevented the lard-like food products from mounting to prices even higher than those current at the present time.

\* \* \*

Up to the time of Burchenal's inventions such a thing as a hydrogenized food industry, or a hydrogenized food of any kind had absolutely no existence. It is to Burchenal, and Burchenal alone, that Procter & Gamble owed the knowledge enabling them to introduce and establish the hydrogenized food industry. The success of that industry is startling, and the benefit to mankind in the enlargement of food products is unbounded. The various witnesses in this case coming from the other concerns in this industry, such as Swift & Co. and this defendant, and the Ward Company, had to acknowledge that they knew of no industry of this kind anterior to its being established by Procter & Gamble under the Burchenal inventions.

#### NOVELTY

The prior art consisted of cotton seed oil (1) liquid, (2) solid or hard.

The liquid cotton seed oil had a melting point of about zero C., and the only melting point for the solid hard cotton seed oil given in the prior patents and publications was the 56 to 60 C. given by Paal & Roth in the *Berichte* of 1909, Vol. 42. They described it in two ways, as follows: "A yellowish white, brittle mass which melted at 56° to 60°." "Brittle mass, nearly white in color, which melted at 57° to 60°."

Semi-solid or lard-like cotton seed oil was new.

Defendant contends that in the progressive hydrogenizing from the liquid to the solid, the oil passed through the semi-solid state, and that some of the samples taken for testing would have been semi-solid. This fact is immaterial in the eye of the patent law under the following propositions:

1. An incidental production while in pursuit of another object, and not exciting attention, or supposed to possess any value, does not constitute an anticipation.
2. A production not in the food product art cannot anticipate.
3. A production, the qualities of which were not recognized for the purpose of the patent, does not anticipate.
4. A change, however slight, which capacitates a new result, differentiates from an anticipation.

The samples taken in the course of the prior production of the hard solid substance, if any, were in minute quantities in the crude state, and were thrown away as soon as tested. Not being intended for a food product they were not filtered to remove the catalyst, nor deodorized, nor chilled.

It appears that the only industrial use made of the knowledge contained in the prior art patents and publications was in soap making. Burchenal testifies that when he visited the Crossfields in Europe they were using it for soap making (Ans. 219), and when Kayser came to this country from Europe the only

use he reported was for soap making (Ans. 267 and 318). Notwithstanding the fact that the Normann patent was in 1903, and that therefore the hydrogenizing of oil had existed for years, there does not appear to have been even a suspicion either in the patents or publications, or in industrial use of its having any application to the art of food products whatsoever prior to Burchenal's conception.

The prior patents and publications are all in the same category. Their sole aim was to produce saturation. This appears on their face.

\* \* \*

It must be perfectly manifest to the court that the idea that a semi-solid, produced by stopping the hydrogenizing at that point, would have utility, never entered the mind of any one until Burchenal, much less that it or any other degree of hydrogenizing would have any application in the food product art.

Not only this, but Dr. Baskerville also points out that the knowledge of the process of hydrogenation as it existed prior to the date of the Burchenal invention would have tended to repel the idea that the product might be edible. He says in answer to Q. 186, Rec., page 752, as follows:

In the Normann British patent No. 1,515, of 1903, there appears on Page 2 of the typewritten copy submitted the following:

"Apart from the formation of small quantities of nickel soap, which may be easily decomposed by dilute mineral acids."

That indicates that the product contained something which is not regarded as suitable for food and would require special treatment for the removal of nickel soaps, a treatment with an acid.

In the communication of Paal & Roth, from the article occurring in *Berichte der Deutschen Chemischen Gesellschaft*, Volume 42, beginning at Page 1541, of 1909, there occurs on Page 1 of the translation submitted the following:

"The hydrogenation of the esters of the unsaturated fatty acids, whereby esters of saturated fatty acids were produced, led to a deep-seated change in the properties of the fats, the new products being pulverizable, crystalline masses."

On the same page, at the bottom, and at the top of Page 2, appears the following:

"In accomplishing this, the remarkable fact was established that not only were the glycerine esters of unsaturated acids hydrogenated but also certain other non-fatty, saponifiable, companion substances which are present to a slight extent in the original fats.

"In our last communication we stated that the reduced cod liver oil, with its iodine number 3, no longer showed the characteristic color reaction of this oil which depends on the presence of lipochromes. Similarly, observations were made with sesame and with cottonseed oil."

Further down the page appears the following:

"Similarly, the very poisonous croton-oil was converted by hydrogenation into a perfectly non-poisonous tallow."

On page 3 in the same article there appears the following:

"We found again, as mentioned in the former paper, that for the complete hydrogenation of all the fats more hydrogen was required than was

theoretically necessary, as indicated by the iodine number of the original fat. In some cases this excess consumption of hydrogen was very considerable. Moreover, we could repeatedly confirm the fact that although more hydrogen had been taken up than was to be expected from the original iodine number, so that one would not have expected any more unsaturated acids to be present, still the hydrogenated fat showed an iodine number, very small to be sure in some cases.

"Naturally the simplest way to account for this excess consumption of hydrogen was to assume leakage from the apparatus. This, however, is contradicted by the fact that after a while the volume of hydrogen remained constant which would not be the case if there was any chance of leakage. For this reason, the only way to account for the excess hydrogen is to assume that some other reduction took place, as, for example, the reduction of glycerides of the oxy-fatty acids or a reduction cleavage of the glycerides into aldehyde and alcohol."

On Page 7 there appears the following:

"As it was of interest to study the physiological action of both the partially and completely hydrogenated oil, two other reduction experiments were performed."

In this connection I wish to state that one would have been in the dark and would not have known what might be present in partially hydrogenated material. It might have been poisonous, it might have been harmless. In fact, evidently Paal was mindful of this, because he took precautions to have physiological experiments made. This is indicated on Page 13 of this article of the translation:

"Cottonseed oil gives the Bechli and Halphen tests which are used in food chemistry for detecting the presence of this oil when used as an adulterant. The cause of the first reaction is the presence of a small quantity of unsaponifiable constituent which has not been characterized further chemically except that it is capable of reducing an alcoholic-etheral solution of silver nitrate to metallic silver. The constituent of cottonseed oil which causes the Halphen reaction (red coloration on heating with a mixture of amyl alcohol and sulphur dissolved in carbon disulfide) is also found in the unsaponifiable part of cottonseed oil."

On page 14 there appears the following:

"Both the hydrogenated products which we obtained from cotton-seed oil failed to give either of the above tests. This shows that the unsaponifiable constituents as well as the unsaturated fatty acids are acted upon by the catalytic reduction, and in this case the effect was permanent, for negative tests were obtained even after the products had stood for ten months."

\* \* \*

#### INFRINGEMENT

The infringing Kream-Krisp is represented in this case by the can stipulated, with its labels and pamphlet circulars.

That it is a *lard-like food product* appears from inspection, and is clearly implied by its label:

Dr. Baskerville confirms this by testifying that it is a lard-like food product and a substitute for Crisco.

That it is *homogeneous* is clear upon inspection. Dr. Baskerville so testifies, and is not denied in the record.

That it was made from cotton seed oil by the addition of hydrogen is stipulated.

That its hydrogenizing is incomplete in the sense of the patent in suit appears from its semi-solid consistency.

\* \* \*

In any continuous process like defendant's Moore process, as well as in any batch process, the three factors of hydrogenizing, the oil, hydrogen, and the catalyst, are brought together, and both defendant's process and the process described in the Burchenal patent stop the hydrogenizing at the semi-solid range by limiting the time that they remain in contact. Dr. Walker admitted that this was done in defendant's process by regulating the velocity of the flow of oil through the catalyzer. The result of the defendant's operation is described by Dr. Walker as he understands it, Ans. 125; Rec., p. 526, and immediately in the next answer he admits that in the batch process the result is the same, except as to percentages. If any cotton seed oil and hydrogen get through defendant's catalyzer without being catalyzed, the same would be true if the batch process were conducted carelessly with insufficient agitation.

The Moore patent shows that no substantial amount of hydrogen and oil gets through the catalyst without being catalyzed when the apparatus is properly constructed, because it acknowledges that such might occur if the diaphragm were cracked. It states that this difficulty has been overcome. It says (patent No. 1,184,480, p. 4, line 45): "One of the difficulties that I have met with practically in the operation of an apparatus of this character, having a diaphragm of large area has been due to the occasional cracking of the catalytic layer, and also due to the expansion of the casing which forms cracks or spaces at the outer edges of the diaphragm, through all of which cracks and spaces the hydrogen escapes into the lower compartment thereby permitting some of the oil to pass through without being reduced, and so reducing the pressure above the diaphragm that the gas will pass therethrough in only limited quantities. I have overcome this difficulty by incorporating with the layer of catalytic material long-fibered asbestos, as hereinbefore explained, which I find prevents the formation of cracks. The difficulty due to the expansion of the casing has been overcome by the provision of the ring 51 which clamps the margins of the portions of the diaphragm against the outer shell."

Defendant's evidence shows that the diaphragm used by it is built according to this improvement, and is therefore such as to overcome, as the Moore patent says, the difficulty of "permitting some of the oil to pass through without being reduced." This accounts for the fact that in most all of the specimens of Kream-Krisp tested by plaintiff there was no unchanged cotton seed oil at all, and in those where there was any that it was a mere trace, such as about 1 per cent. It also accounts for the fact that in defendant's circulars they assert that Kream-Krisp contains no unchanged oil.

#### THE HALPHEN TEST

The patent in suit describing the specific product claimed in claim 4, says (p. 2, line 7): "it shows no free cottonseed oil when subjected to the Halphen test." Defendant's witness Richter testified that although the sample of Kream-

Krisp in evidence showed no response to this test, yet all other samples of defendant's product which he had tested did respond thereto. Presumably this testimony was intended to have some bearing on the question of infringement. But while this test is specified in Claim 4, it is omitted from claims 1 and 2 in suit and is therefore irrelevant to the present issue.

The Halphen test, moreover, is irrelevant and immaterial from any practical standpoint. It is admitted by everybody that the substance which reacts in showing the test is so minute that no one has ever determined exactly what it is. It is also proved by Dr. Baskerville, Ans. 25, Rec., p. 434, and Morrison, Ans. 53, Rec., p. 781, that it will detect the presence of a mere trace of cotton seed oil, as little as 1 per cent or less. Therefore the fact that a body responds to the Halphen test does not show that it contains more than a trace of cotton seed oil, such as could not possibly make any practical difference.

Dr. Baskerville testifies, Rec. p. 747, Ans. 160-164, that he tested three different specimens of Kream-Krisp obtained in different parts of the country, and that none of them responded to the Halphen test. Morrison, Rec., p. 781, Ans. 49-53, testifies that he had tested about a dozen specimens of Kream-Krisp and that the majority did not respond to the Halphen test, and the minority that did respond gave so faint a response as to indicate the presence of only a trace, such as 1 per cent or less, of cotton seed oil.

Richter is the only one who has testified on this point for defendant, and he does not undertake to say the presence of how much cotton seed oil his tests indicated, so that it is fair to assume that it did not indicate any more than the trace which Morrison testified to. It is admitted and asserted by defendant's circulars that Kream-Krisp does not contain any unconverted oil at all, as shown by the following quotations:

Kream-Krisp although made exclusively from highly refined vegetable oil, contains no oil itself. The oil is completely changed by hydrogenation under the influence of heat to a butter-like substance.

Kream-Krisp although made from highly refined vegetable oil, contains no oil itself. The oil is completely changed to a butter-like substance.

The conclusion is that even if Kream-Krisp does in some cases respond to the Halphen test it is immaterial both from the standpoint of claims 1 and 2, and from the practical standpoint.

\* \* \*

In almost all chemical cases, particularly those in organic chemistry, one side or the other rambles off into theoretical and impractical considerations which are totally unnecessary for the decision, and which the experts wrangle about until the record of what should be a very simple matter becomes very much confused. We are sorry to say that this case is no exception to the above.

\* \* \*

These theories in this case are embodied in the triangular charts produced by defendants' expert, upon which their depositions as to both anticipation and non-infringement are based.

Dr. Baskerville points out that defendants' triangular charts would be unobjectionable if we were investigating the proportional constituents of bodies having **only three components**, such as, linolin, olein and stearin, because then the

three components would be properly represented by the three sides of the triangle. But where the proportions of components are under consideration in substances having more than three, the triangle is obviously inappropriate, and any conclusions based upon the triangulation must be misleading.

The proof of this is easy, because upon a moment's consideration it will be apparent that from a practical standpoint, defendants' triangular charts resulted in *reductio ad absurdum*.

The absurd conclusion is reached that of three substances, two of which (Crisco and Kream-Krisp) are semi-solid and one of which (cotton seed oil) is liquid, the two semi-solid substances are further away from each other than one of them is from the liquid substance.

\* \* \*

Dr. Baskerville summarizes the reason why he chose stearin as the basis of his charts as follows, Ans., 309, Rec., p. 775: (1) "It is the specific substance that is mentioned in the Burchenal patent to bring about congealing . . ." (2) "It is known to be the factor which is involved in making lard compounds out of these hydrogenized products." (3) "It is quite evident that what we obtained, the results have shown, is in accord with the known facts." (4) "Olein and linolin are liquids, they are liquids through a wide range of temperatures, and we are considering here substances at the ordinary temperatures."

We will now take up each of these reasons and explain it more in detail.

The statements of the patent bearing upon Dr. Baskerville's first reason are as follows:

"Saturated fats, however, serve the purpose of congealing the shortening within the food, and thus retain it equally distributed throughout the whole" p. 1, line 50.

"Sufficient stearin to make the product congeal at ordinary temperatures" p. 1, line 72.

"Enough stearin to make the product congeal at ordinary temperatures" p. 2, line 24.

In all of the above statements the congealing or semi-solidifying which is the attribute making the product lard-like is associated with the saturated fats, particularly stearin, which represents the increase of saturated fat from hydrogenizing. The statement first above quoted that the saturated fats "serve the purpose of congealing the shortening within the food, and thus retain it equally distributed throughout the whole" appears from the testimony to be the very attribute which, from a practical standpoint, is the reason why the semi-solid or lard-like shortening is preferred by cooks to the liquid shortening. Every witness on both sides who has mentioned the subject has said that the liquid is inferior because of the difficulty in getting it equally distributed throughout the dough.

Since, therefore, the patent specification and the cook agree in laying so much stress upon the saturated fats and their congealing or semi-solidifying effect, in contradistinction to the liquid, there is certainly every reason for dividing the product into the solid and liquid ingredients in making a chart.

Dr. Baskerville's second reason is that the saturated fats are known to be the factor which is involved in making lard compounds out of the hydrogenized product. What he means here is that in the mixtures of Burchenal's companion



patent No. 1,135,935 the practical value of the mixture over and above liquid cotton seed oil is due to the fact that the liquid ingredients on the one hand and the solid ingredients on the other hand result in that semi-solidity, or lard-like consistency, or congealed condition at ordinary temperatures, which proves to be so desirable in mixing the dough.

Dr. Baskerville's third reason is that the result he has shown by his charts is in accord with the known facts. He means here that we know that Crisco and Kream-Krisp are close together in respect to their semi-solid, lard-like, congealed at ordinary temperatures condition, and that a chart, as his does, which brings them together and separates them on the one hand from things that are liquid, such as cotton seed oil, and things that are solid, on the other, is in accordance with the known facts. Whereas a chart, such as defendants', which separates the semi-solid, lard-like bodies, Crisco and Kream-Krisp, and brings either of them together with a liquid body like the oil, is in opposition to known facts, and as we have stated above, *reductio ad absurdum*.

Dr. Baskerville's fourth reason is that we are considering here substances at the ordinary temperatures, and therefore that it is proper to divide the constituents between those that solidify below ordinary temperatures and those that do not.

Our adversary will refer to the statement of the patent that the proportions are high in olein and low in linolin.

We have already shown by the file contents that these parts of the specification were inserted with claims 5, 6 and 7. They do not affect claims 1 and 2.

But it would be a mistake to suppose that Kream-Krisp is not in the direction of these statements;—it follows them to a degree.

Comparing Kream-Krisp, Crisco and the Burchenal patent product with the cottonseed oil from which they are obtained, they are all lower in linolin, higher in olein, and higher in stearin. Defendant's witness Walker admits this (Ans. 46-51). In other words, relatively to the cottonseed oil from which they are obtained, they are all low in linolin, high in olein, and with enough stearin to be congealed or semi-solid at ordinary temperature.

There is no doubt that Kream-Krisp would be better if it more nearly complied with the proportions of the patent. If it were higher than it is in olein and lower in linolin it would be less liable to oxidation. This is admitted by Dr. Walker, Rec., p. 512, Ans. 59, and is testified to by Morrison, Rec., p. 782, Ans. 59. But the fact that Kream-Krisp is an inferior following of the patent does not relieve it from infringement, because the law is to the contrary.

\* \* \*

The fundamental error of the attack on the patent from the chemical side is that it proposes to confine the invention of the Burchenal patent to his preferred product as set forth in claims 5 to 7, and entirely fails to distinguish between the product as covered in claims 1 and 2 and the preferred form of the claims not in issue.

The patent has to do with chemically changing the complex glycerides of the vegetable oil so as to vary the proportions of the liquid and solid components in the oil itself, and thus to produce a food product semi-solid and lard-like. It aims to produce this change not as in the companion Burchenal patent by solidifying or saturating the whole body of oil with hydrogen and thus obtaining a semi-solid by dissolving the hard material in additional untreated oil, but by

creating the necessary solid at the expense of the liquids in the oil itself until the proper consistency of lard is obtained. This conversion and chemical change of the liquid components to obtain the lard-like product is the essence of the patent in suit, and it is fully and properly protected by the first two claims. The change in the components of the oil could not be protected by claims more in detail which specify to what extent the components should be changed, or proper protection be given to the Burchenal invention in issue by limiting him to specific components, as is abundantly evidenced in this very case.

\* \* \*

The point was to raise the melting point of the original oil so that it would be semi-solid, plastic and lard-like at normal temperatures. Burchenal was not concerned, in this view of the case, with whether all, or a large part of, the linolin was changed to olein or whether the linolin was less reduced and the olein less increased and the desired consistency was obtained by increasing the stearin. The new product must have those proportions of liquid and solids chemically created by the treatment to give the desired lard-like quality. The change in the oil itself so that no original oil remained was the essential thing. To what extent the components were changed so that the desired product was obtained was a mere matter of degree.

There were a number of old methods of hydrogenating. The batch methods of Normann & Kayser, the continuous methods of Bedford & Williams, and Erdman. In Normann & Kayser, the hydrogen bubbled through the oil and the whole mass of oil and catalyst was treated continuously with the hydrogen. In the Bedford & Williams method the oil was run through or over the catalyst supported on pumice stone, either in an atmosphere of hydrogen or the hydrogen was sprayed over the fixed catalyst. In Erdman the oil was sprayed by the incoming hydrogen just as in the defendant's apparatus against a rotating cylinder plated with the catalyst, and the treated oil was then run through a body of catalyst in the bottom of the vessel.

All of the old methods fully saturated the materials. They converted all of the linolin and all of the olein into stearin. Burchenal, through Kayser, was familiar with the batch method. He therefore preferred that method of treatment. Burchenal, however, had a new product in view. He did not change all of the linolin and olein to stearin, but carried on the conversion until he had made enough solid or saturated material to give him his lard-like hydrogenated food product. Because the hydrogenization process was old in no way negated the novelty of his new product, obtained by his special manipulation of that process.

Burchenal obtained a specific product high in olein, low in linolin and with only enough added stearin to give the proper lard-like material, which he covered in claims 3-7. If Burchenal had preferred the Bedford & Williams process, where the oil is passed continuously across or through the fixed catalyst supported on pieces of pumice, he would have obtained, by special manipulation of that process, a product which, while responding fully to his invention, might probably not have presented the specific changes called for in the specific final claims of his patent. So, if he had preferred the Erdman process of spraying the oil by the hydrogen against a rotating catalyzed cylinder and he had specially manipulated that process, he might have obtained still a third species of his invention.

Then Moore, of the defendant company, in order to make the Burchenal product by chemically changing the component glycerides and creating sufficient stearin to obtain the desired lard-like consistency, designs a modified Erdman machine of the continuous Bedford & Williams type. In this machine he rotates a spray of hydrogen and oil over a fixed diaphragm of catalyst, and in this way has a small portion of the oil and catalytic nickel in contact on a moving pie-shaped sector portion of his diaphragm, say about  $\frac{1}{10}$  of the disk, and a much greater portion of his oil, catalyst and hydrogen in contact through the remaining  $\frac{9}{10}$  of his diaphragm.

This Moore machine was designed a number of years after Burchenal entered the field, and for the very purpose of producing an incompletely hydrogenized, homogeneous, lard-like food product. Moore, by the use of his machine, thus produces exactly the product of the patent, but he obtains a different specific change in the components. The only difference between the product produced in the Moore machine and that produced by Burchenal is the degree of variation of the component glycerides, so that the product of the Berlin Mills Co. is not in accordance with the preference of Burchenal.

#### THE TRIANGULAR CHARTS

In order to show that the components of the mixed glycerides in defendant's product are different from the specific components of plaintiff's patent, a fact which we do not and never have denied, the defense has introduced its triangular charts to visualize the admitted difference between the species of product of the final claims of the patent in suit and the species of defendant's product, both of which products, however, fall directly under the first and second claims of Burchenal, which claims define the broad and fundamental distinction between the patented product and anything which preceded it.

The triangular chart can only visualize the similarity or difference between materials having three components. It is therefore grievously misleading to attempt to compare products of four or more components unless we can group the components into three parts.

The essential constituents which make the product lard-like as distinguished from a liquid are the added hard materials, not the changed proportions of the liquids. The defendant has used its charts to visualize the difference in the proportions of the liquid glycerides, and as the proportions of the liquid glycerides are admittedly different the defendant is able to place plaintiff's and defendant's products far apart on its charts, but at the same time it has been forced to demonstrate how untrustworthy is its method, because, by this method the two semi-solids, Crisco and Kream Krisp, are located very much further apart on their charts than one of these products is distant from the liquid cotton-seed oil.

If the triangular chart is to be used at all we should obviously plot the three constituents that are the essentials in the products being compared. These three essentials are, (a) the liquid components, (b) the original hard component (not sufficient to alter the liquid form), and (c) the added hard material (which is sufficient to convert to a semi-solid condition).

In order to compare the products in respect to these essentials the plaintiff has introduced its chart IV, which is identical with the defendant's charts 10 and 14, and plaintiff has plotted the various products in accordance with these essentials, making one side of the triangle represent the ordinary solid-fats,

another side the added solid fats and the third side the liquid fats (as the plaintiff did not have the enlarged charts of defendants, the lines which divide the defendant's charts 10 and 14 are not all placed on chart IV.).

As indicated on chart IV, when the various products to be compared are plotted, the cotton-seed oil (as there are no added solid fats) appears on the base line and the Crisco and Kream Krisp products measured by the amount of added solids are brought close together as they should be, while Defendant's Exhibit L 7, which is not any recognized or intentional product of the prior art, appears some distance from Kream Krisp and Crisco, and with the Kayser product, Exhibit III, near the top of the chart.

These various products have been plotted with reference to an average cotton-seed oil which contains, according to the evidence, about 21.5% of solid fats.

In the Burchenal patent a cotton-seed oil of only 17 per cent of solid fats is mentioned which, from the Morrison testimony, would appear to be an unusual oil, as produced generally in this country, although it appears that the proportion of solid fats in ordinary cotton-seed oil of commerce ranges from 18 per cent to 25 per cent.

We have theretofore indicated on chart IV, the Burchenal product based on this rather unusual cotton-seed oil with only 17 per cent of solid fat.

It seems immaterial to discuss whether Burchenal in testing the cotton-seed oil had an unusual grade or not, because it is very evident from the specification that what he proposed was a product in which from 3 per cent. of solid fats were added by the hydrogenization in order to give the desired lard-like food product. The patent states:

It contains from 20 per cent. to 25 per cent. of fully saturated glycerids . . . while the cottonseed oil before treatment contained 17 per cent. saturated fats.

It therefore seems evident that when the various products under investigation are plotted with reference to the essential components, dividing them into three parts, that is, (a) the original solid fats, (b) the added solid fats and (c) the liquid fats, plaintiff's product Crisco and defendant's product Kream Krisp are brought very close together with the Kream Krisp actually lying between the extremes of the two Crisco products in evidence; all three of the products lying between the extremes of the solid fats to be added in accordance with the patent as illustrated in Complainant's Exhibit Chart IV.

As it is the melting point taken in connection with the added solid fats that determines the semi-solid character of the patented product set forth in claims 1 and 2 and determines whether the product of the defendant comes within the limitations of the terms of those claims, the plaintiff has introduced its chart V, in which, on a vertical line, it has indicated the percentages of added solid fats from 0 to 100, and on a horizontal line the melting points, Centigrade scale.

In chart V the position of cotton-seed oil and the Crisco products, Kream Krisp, the Burchenal product based on a cottonseed oil of only 17 per cent. original solid fats, are indicated also the product L 7 and Kayser Exhibit 3. By running a line through the proximate positions of these products as plotted on chart V, we obtain a curved line which at the lower end approximates to the horizontal and at the upper end approximates to the vertical, giving a rather sharp bend between a range of melting points 32 to 40 as specified by Burchenal, and showing Kream Krisp and Crisco in almost the same location at the most

pronounced portion of the curve. It is very evident from an examination of this chart that all the homogeneous, lard-like, semi-solid products will fall in a little group at the bend of the curve, which visually indicates the transition point from liquid to semi-solid.

There is still another method of comparing the patented products with the product of defendant (this is shown in Plaintiff's chart VI) in which lines are drawn to indicate the proportions of the liquid fats and the solid fats in the various products, all that portion of the chart lying below the indicated line of any particular product representing the solid components, and that portion above the line, the liquid components. Then, by taking the melting points of the various products we are again able to plot these products, and the line upon which the products lie, as determined by the melting point, is the same as the curved line illustrated in plaintiff's chart V.

All these methods lead to a common result, that is to say, that by starting with cotton-seed oil and creating in the oil additional solids, by partial hydrogenation, a homogeneous semi-solid lard-like product is produced.

\* \* \*

#### PRIOR SHORTENING MATERIALS

The defendant has taken a large amount of testimony to prove that cotton-seed oil itself was an edible product and had been used extensively for cooking purposes, and also that compounds of cotton-seed oil with beef fats (oleo-stearin), had been very largely manufactured and sold for this purpose. The object of this evidence is not quite clear, but we assume that its purpose was something derogatory to the plaintiff's case, or to the patentability of the Burchenal invention. Neither of these facts, if true (and we have no reason to question their truth), is material to the present case, because it is not contended that either cotton-seed oil or oleo-stearin compounds of the same, anticipate the invention of the claims in suit. It has never been contended on the part of Burchenal that he first suggested the use of cotton-seed oil either as an edible product or as a cooking material. But the prior knowledge and use of these materials do not change the fact that Burchenal produced from cotton-seed oil a new material which has enormously extended the use of cotton-seed oil in the food industry, and which has large advantages over its use either alone or combined with oleo-stearin. Moreover, the partially hydrogenated product of the patent in suit is recognized in the commercial world as a distinctly different product from any other cooking material on the market (see Richardson, in answer to questions by the Court).

In connection with this evidence of the prior use of cottonseed oil and oleo-stearin compounds, defendant examined Dr. Bacon as to the subsequent use by the Ward Baking Company in making bread, of a shortening material consisting of hard hydrogenized cotton-seed oil like plaintiff's Exhibit III, finely ground and thoroughly mixed with flour. It developed in the course of the cross-examination of Dr. Bacon that this material was patented to one Esterbrook, the patent being owned by the Ward Baking Co. From the claims of this patent it appears that the invention consisted merely of comminuted hardened oil mixed with flour. It is used by mixing it in proper proportions with the flour of which the bread is made. The evidence with regard to this material shows

that it was not equivalent to the hydrogenated product of the patent in suit and that it was of much later date, Dr. Bacon testifying that the Ward Company began using it in 1914 or 1915.

Both the cotton-seed oil and the Ward-Esterbrook material, one a liquid and the other a dry powder, require to be mixed very thoroughly with the flour with which it is combined for cooking, and the merit of each material depends upon the thoroughness of this mixing. It has been shown by the testimony of Miss Hanko on the part of plaintiff in rebuttal, that this fact constitutes a very great objection to the use of these materials, and, while it is possible to utilize them for shortening material in place of lard and lard compositions, such practice is not within the range of the patience and ability of the ordinary housewife.

The most serious objection to the use of the liquid cottonseed oil as a shortening material is the fact that it affords no moisture within the dough, while it decreases by 50 per cent. the amount of water or milk required to make the proper consistency of the batter, and, as a result, the steam generated in cooking which is needed for raising the dough to give it its light and flaky character when cooked, is absent. The consequence is that it is necessary to use expensive baking powder in connection with the oil to accomplish this result.

As to the hard material, it cannot be used in frying without leaving a coating on the product, and the hardened material is indigestible because it cannot be acted upon in the digestive processes until it is in melted condition. If it remains unmelted at the body temperature, all the authorities hold that to that extent it is indigestible, or at least is very much harder to digest than the semi-solid cooking fats.

It plainly appears from the evidence that the partially hydrogenized semi-solid product is the best of all the cooking materials discussed in the case. In Part I., *supra*, we have recited from the patent in suit various advantages it has over the best leaf lard, and necessarily therefore over compounds of cotton-seed oil and oleo-stearin. Mr. Morrison was examined by the plaintiff in rebuttal on these points, and states with regard to such advantages that in his opinion such statements of the patent were true when the application was filed, and that they are also true to-day (Morrison, Rec., p. 782, Qs. 61-70). Thus, he says that the oil does not make the best shortening, that the hard fats were not as digestible as liquid fats, that the semi-solid of the patent in suit more closely resembles lard than do the commercial mixtures of cotton-seed oil and oleo-stearin, that in many respects the semi-solid product is superior to leaf lard as a shortening, that it is not so liable to become rancid and that the product can be heated to a considerably higher temperature without smoking or burning.

The testimony of Guy B. Taylor as to the commercial introduction and general acceptance of plaintiff's patented product shows sales rising from two and half million pounds during the latter part of 1911 progressively from year to year up to sixty million pounds in 1916. This is eloquent testimony to the intrinsic value of the product and its relative merit as to prior and competing materials.

Defendant is not in a position to assert that the hydrogenized semi-solid product is not of superior merit to the various cooking materials to which the evidence above referred to relates, for in its pamphlets in evidence it takes the ground that its product Kream Krisp, which is a hydrogenized semi-solid made from cotton-seed oil, is superior not only to lard, but also to compounds of

cotton-seed oil and oleo-stearin; indeed, to all other shortening materials on the market, laying particular stress upon the fact that it will not turn rancid, does away with beef stearin, has a high smoking point, is free from adulteration and contains no hard fats or oil, but is completely changed by hydrogenization to a butter-like consistency, has a low melting point and is easily assimilated by the digestive organs.

No evidence has been offered on the part of the defendant questioning the merit in any of the above particulars of plaintiff's patented product over these prior cooking materials, nor has it been claimed that defendant's hydrogenized product is any better or different in these respects from that of the plaintiff.

We think it is quite evident that not only is this testimony offered by defendant in regard to the character and use of these other cooking or shortening materials, wholly immaterial to the present issue, but that the record establishes the superior merit of the plaintiff's partially hydrogenized semi-solid product, not only over these prior materials, but also over the best leaf lard itself.

#### CONCLUSION

In conclusion, we submit that Burchenal was the first to conceive and utilize hydrogenated cotton seed or other vegetable oil for edible purposes; that he was the original and first inventor of an homogeneous lard like food product, consisting of an incompletely hydrogenized vegetable oil, as set forth in claims 1 and 2 in suit, and the father of the hydrogenized oil food industry; that the plaintiff was the first to introduce the said food product into public use and has effected a very wide and extensive introduction of the same and thereby conferred a great benefit on the public; that the invention set forth in claims 1 and 2 in suit is new, not having been publicly used, or patented, or described in any printed publication, prior to the invention or discovery thereof by Burchenal; that the claims in suit are not limited, either by their own terms, or by the prior art, or by the accepted rules of construction, to the specific product set forth in the specification and claimed in the other claims of the patent; that plaintiff by reason of the premises is entitled to a broad construction of said claims in suit; that defendant by the manufacture and sale of "Kream Krisp" has infringed the claims in suit; and that, therefore, the plaintiff is entitled to a decree as prayed in the bill.

April 28, 1917.

KERR, PAGE, COOPER & HAYWARD,  
Solicitors for Plaintiff.

LIVINGSTON GIFFORD,  
ALFRED M. ALLEN,  
THOMPSON B. KERR,  
Of Counsel.

(16261)

UNITED STATES DISTRICT COURT.  
SOUTHERN DISTRICT OF NEW YORK.

PROCTER & GAMBLE COMPANY,  
*Plaintiff.*

vs.

BERLIN MILLS COMPANY,  
*Defendant.*

In Equity, No. 13-100.  
On Burchenal Patent No. 1,135,351.

BRIEF FOR DEFENDANT.

JOHN C. PENNIE,  
*Solicitor for Defendant.*

MARCUS B. MAY,  
JOHN C. PENNIE,  
*Counsel for Defendant.*

FOREWORD

This case involves food fats, one of the three life sustaining elements, which consist of proteins, carbohydrates and fats.

The use of fats and oils of animal and vegetable origin is primarily that of a food, although to a more limited extent such fats are employed for the manufacture of soap, candles, lubricants and illuminants. Edible fats may be divided into table and culinary fats. "Table fats are those like butter and table oils, which are most commonly used as an accompaniment to food to secure a desired flavor or texture, and culinary or cooking fats are those which are incorporated with other foods (as shortening) or used as a medium for cooking foods, as in frying."

The alleged new product which forms the subject matter of the patent in suit, belongs to the second class, to wit, culinary or cooking fats; and

it is at last an article which pertains to the cooking art; an art, if it may be properly called an art, which is as old as the discovery of the uses of fire, and as varied in its exemplifications as the sands of the sea . . .

(Lurton, C. J. in *Sanitas Nut Food Co. vs. Voigt* 139 Fed., 551, 553.

It is said to be a "food product consisting of a vegetable oil, preferably cottonseed oil, partially hydrogenized and hardened to a homogeneous white or yellowish semi-solid closely simulating lard." As will be shown, there have been on the market for many years as staple culinary fats, food products consisting of cottonseed oil hardened to a homogeneous white or yellowish semi-solid closely simulating lard by the addition of stiffening agents, such as oleo-stearine or a hard vegetable fat. As illustrating the extent to which such "lard compounds" or "lard substitutes" as they are called, are produced, the record shows that



Swift & Company alone manufacture and sell between 250,000,000 and 500,000,000 pounds annually of such food products.

The stiffening or hardening of cottonseed oil by hydrogenation is not claimed as new in the patent in suit, for this was common property, and semi-solid fats produced by the hydrogenation of cottonseed and other vegetable and animal oils were also common property, before the alleged invention of the patent in suit, as the patentee concedes.

In the very nature of things it appears at the outset that the product of the patent in suit involves only the selection of a known fat for a use "as old as the discovery of the uses of fire."

#### PARTIES

The plaintiff, Procter & Gamble Company, an Ohio corporation.

\* \* \*

The main business of the plaintiff was and is the manufacture of soap, and since March, 1909, it has been also engaged in the manufacture of a lard substitute (Flake White) which however is not the alleged new product of the patent in suit, and since May, 1911, it has also been engaged in the manufacture of Crisco.

The defendant, Berlin Mills Company, is a Maine corporation having mills at Berlin, New Hampshire, for the manufacture of paper and wood pulp. For the purpose of utilizing a by-product—hydrogen—produced in the manufacture of bleach, it built a plant for the hydrogenation of oils, and by September, 1914, placed upon the market a lard substitute, Kream Krisp, which is alleged to infringe the patent in suit. This material is produced by a novel process and apparatus which are covered by defendant's patents.

#### DEFENSES

In this case, the defendant relies upon two defenses, to wit:

- (1) The patent in suit is invalid and void; and
- (2) the defendant's product does not infringe the claims sued on.

Under the first defense, the defendant submits that the patent is invalid and void:

(a) because the patentee failed to comply with the provisions of Section 4888, U. S. Revised Statutes, which require such a written description of the product claimed and the method or producing it as will enable one skilled in the art without experiment "to make, construct, compound and use the same";

(b) because of new matter inserted in the specification and claims during the prosecution of the application which resulted in the issuance of the patent in suit;

(c) because if there be any modicum of invention in the claims of the patent in suit—which the defendant denies—it is not the invention of the patentee, John J. Burchenal, but is the invention of Edwin Cuno Kayser, who disclosed it to said Burchenal; and

(d) for want of patentable subject-matter.

Under the second defense, that of non-infringement, the defendant urges:

(a) That by reason of restrictions and limitations imposed upon the specification and claims in order to secure their allowance, the claims must be construed

narrowly to a product having certain definite physical and chemical constants different from those of defendant's product—Kream Krisp;

(b) that Kream Krisp is not a homogeneous lard-like food product consisting of incompletely hydrogenized vegetable (cottonseed) oil, within the meaning of the claims;

(c) that the claims must be limited to a product produced by the process described in the patent specification, and, since Kream Krisp is produced by a different process, it does not infringe; particularly as

(1) defendant's process cannot produce the product described in the patent in suit; and

(2) the process described in the patent in suit cannot produce defendant's product.

#### THE PATENT IN SUIT

The patent in suit to John J. Burchenal, No. 1,135,351, was applied for on November 10, 1910, and was issued April 13, 1915. It is not contended that defendant infringes claims 3 to 7, inclusive, which are directed to the product specifically described in the specification, the plaintiff relying only on claims 1 and 2.

The specification describes a process of hydrogenating cottonseed oil, by agitating a mixture of oil and catalytic nickel, when heated to a temperature of about 155° C. in the presence of an atmosphere of hydrogen, and stopping the reaction when the product on cooling is a white or yellowish semi-solid.

It is conceded by Burchenal that he is not the inventor of that process of hydrogenation described in his specification, and is not the inventor or discoverer of the semi-solid fatty products produced by such process.

The Kayser patents, 1,004,035 and 1,008,474, which are conceded to be prior art by Burchenal, describe in detail the process briefly referred to in the Burchenal patent specification and also describe the production of both solid and *semi-solid* products of any desired consistency by the hydrogenation of cottonseed oil. Various other patents and publications of the prior art, as will be shown, describe the hydrogenation of cottonseed and other oils into both solid and semi-solid products or fats.

The Burchenal patent presents no claim for the process of hydrogenation, and no claim *in haec verbis* for "a semi-solid product produced by the hydrogenation of cottonseed or other vegetable oil." The two claims in suit, however, specify

A homogeneous lard-like food product consisting of an incompletely hydrogenized vegetable (cottonseed) oil;

and by referring further to the specification, there is given a description of this specific food product, to wit: one "which is high in olein, low in linolin and lesser saturated fats and with only enough stearine to make the product congeal at ordinary temperatures" page 2, lines 22-27; or, more especially, one containing "twenty to twenty-five per cent. of fully saturated glycerids, from five to ten per cent. linolin and from sixty-five to seventy-five per cent. olein.

The specification, however, is silent as to any method for producing this particular "lard-like" food product. It assumes that such product will be produced by the particular process set forth in lines 80-92, page 1 of the specifica-

tion. It assumes, apparently, that the semi-solid product produced by that process will be subjected to the same treatment that fats are ordinarily subjected in making lard or lard compounds, for the specification describes no after-treatment of any kind to give to the product the salve-like consistency of lard, or the appearance of Crisco, so-called. The specification does not suggest the clarifying, deodorizing, refrigerating and aerating processes to which lard substitutes are subjected. D. R., 70-71, Qs488-495. Nor does the specification suggest that the cottonseed oil, which is to be treated, should be preliminarily refined. The percentage of catalyst to be used, and the extent of the pressure of hydrogen in the hydrogenating vessel are omitted. All these matters are treated in the patent as immaterial, the only directions given being to stop the process "when the oil has been converted to a product which cools to a white or yellowish semi-solid. . . ." A dilemma is thus presented. Either any white or yellowish semi-solid produced by the hydrogenation of cottonseed oil (for example, that described in the Kayser patents is a "homogeneous lard-like product," containing 20-25% stearin, 65-75% olein and 5-10% linolin; or else the patent fails to describe how the product is to be produced, in accordance with the requirements of Section 4888, U. S. Revised Statutes, as will be hereinafter more fully elaborated.

In the first case it is to be observed that the patent in suit while referring to "a vegetable oil" or to "other vegetable oil," actually describes the treatment of cottonseed oil only, and obviously the product described is only that produced by hydrogenizing cottonseed oil, or else the semi-solid products produced by the hydrogenation of *all* vegetable oils must have the proportions of component glycerides recited in the specification. There is either, therefore, no difference between claims 1 and 2, or else claim 1 is for an abstraction—a generalization—and as such is void or invalid. Claim 2 likewise being for the same product which is defined in the specification as having the certain proportion of component glycerids and the other identifying characteristics noted in the specification, must be limited thereto, or else it, too, is a mere abstraction or generalization and directed to what is manifestly old and open to the public generally.

\* \* \*

Where the patentee fails to enlighten those skilled in the art how to practice the invention he has failed to promote the useful arts, because when his patent expires the public is no better off than if the patent had never been granted.

In the present case, as we shall show, the patentee not only seeks to exclude the public from the enjoyment of rights which the public had acquired from prior inventors and discoverers, but seeks to do this on a patent which is fatally defective,—first, because of the unlawful inclusion of new matter, and, second, because the patentee has failed to disclose to the public any method of producing the product specifically described as having 20-25% stearin, 65-75% olein and 5-10% linolin in its composition, or a product having "a high percentage of olein, a low percentage of linolin and with only enough stearin to cause the product to congeal at ordinary temperatures."

\* \* \*

The record fails to show that the product of the patent in suit has ever been produced commercially even by the plaintiff itself.

## CRISCO

The product Crisco, which the plaintiff manufactures, and which was placed on the market in May, 1911, admittedly does not embody or contain the proportions or percentages of component glycerides which the patentee Burchenal specifies in his patent. The affidavit filed by Burchenal on March 5, 1917, intimates that the product as originally described in his specification as filed, "*would necessarily*" or "*must have*" (to use the Examiner's words) the composition 20-25% stearin, 65-75% olein and 5-10% linolin; and Crisco, therefore, does not contain the alleged invention of the patent in suit. It follows that the extent to which Crisco may have been made and sold, is immaterial to the present case.

Furthermore, Crisco is made in part by secret processes—the secrets of which are "jealously guarded." There is no complete statement in this case as to how "Crisco" is actually manufactured. Defendant's counsel were denied the right to see it made, or the machinery employed in its production, or the processes employed in its manufacture; and no one but the plaintiff knows now how to go about it to produce Crisco.

\* \* \*

Morrison conceded that Crisco does not have the composition recited in the patent in suit.

Patent in Suit		Crisco
range		range
Stearin	20-25%	26-27.3%
Olein	65-75	57.8-52.9
Linolin	5-10	16.2-19.8

Crisco, as thus conceded, does not have the percentage of olein (65-75%) and the percentage of linolin (5-10%) which the product of the patent in suit "*must necessarily*" have, and is not the alleged new product of the patent in suit.

It is obvious, therefore, from this brief survey of the patent in suit, which will be amplified hereinafter with the admissions and concessions of Burchenal and other officers and employees of the plaintiff, that the patent is a menace to the public, that it is a raid on the public rights, and that the Court should declare it void.

This patent in suit is part of a general plan to deprive the public of any right whatever to use hydrogenized fats for culinary purposes. The plaintiff has another patent, No. 1,135,935, issued to Burchenal on April 13, 1915, and which was filed coincidently with the patent in suit. On patent No. 1,135,935, a suit has been brought and is now pending against Swift & Company of Chicago, Richardson, XQ76, T. R., page 563. That patent purports to cover any lard-like edible hydrogenized oil or any edible product comprising a mixture of any hydrogenized oil with any unhydrogenized oil. There are 14 claims, of which the first four read as follows:

1. A lard-like composition comprising edible hydrogenized fatty oil.
2. A lard-like composition comprising edible hydrogenized vegetable oil.
3. An edible oil product, comprising hydrogenized cottonseed oil and edible oily material blending therewith.
4. An edible oil product of lard-like consistency, comprising edible hydrogenized oil and edible oily material blending therewith.

By claiming any lard-like "edible hydrogenized fatty oil" and any oily mixture containing hydrogenized oil in the one patent, and any edible lard-like "partially hydrogenized vegetable oil" in the patent in suit, the plaintiff company apparently seeks to exclude the public from its right to use, for edible or cooking purposes, any hydrogenized oil—and yet Burchenal admittedly did not invent any process of hydrogenation and did not invent or discover either fully or incompletely hydrogenized oil products, and did not invent anything to make such products available for edible or cooking purposes.

\* \* \*

One of the chief concerns of many governments to-day, including our own, is to supply their people with food fats sufficient to sustain life. But this plaintiff is seeking to make private gain from the world need. It asks this Court to aid it in excluding from the use of the public as food products those fats which prior to Burchenal's appearance had already been dedicated to the public for all the purposes to which they might be put by those men to whom belongs the credit of their discovery and production.

\* \* \*

In reviewing the history of hydrogenation, the brief states olein and linolin are both liquids, the latter having a solidification point much lower than the former. The saturated glycerides are solids, and are soluble in the unsaturated glycerides. But of the two unsaturated glycerides, linolin is capable of dissolving or holding in suspension a greater quantity of stearin than is olein. Hence, in those fatty bodies which are solid or semi-solid at ordinary temperatures, the stearin, olein and linolin are in such proportion that the stearin is not in suspension or in solution. The stearin may be either present in larger proportion in the fat than in the oil; or the linolin may be so decreased and consequently the stearin so thrown out of solution as to solidify the mass.

The same phenomenon appears when cottonseed oil, which consists of stearin, olein and linolin, is chilled. As the solvent power of the olein and linolin decreases with the lowering of the temperature, the saturated glycerides appear visibly, and by filtration they may be retained in the filter and the liquid glycerides olein and linolin separated therefrom. Now, when the oil,—say, for example, cottonseed oil, which consists of linolin, olein and stearin (stearin and palmitin grouped together as "stearin"),—is subjected to the "batch method," or Normann method, of hydrogenation, the linolin, which is more unstable of the two unsaturated glycerides, because it has *two* double bonds, is acted on first and is converted to olein. If the hydrogenation is carried on long enough, however, the olein is also affected, and at last both the linolin and the olein are converted into stearin. But during the progress of the reaction, the proportion of olein is gradually increased with the corresponding gradual decrease in linolin, and the viscosity of the oil is gradually increased until it assumes a semi-solid condition. This may or may not be accompanied by an increase in the proportion of stearin. In the patent in suit, for instance, the preferred semi-solid product described therein is said to consist of 23% stearin, 69.5% olein and 7.5% linolin,—or generally 20-25% stearin, 65-75% olein and 5-10% linolin. It is conceded by Dr. Baskerville that cottonseed oil, according to an analysis given by him, may consist of 23.3% stearin, 28.9% olein and 47.8% linolin. Hence, to produce the preferred product of the patent in suit, the 47.8% of linolin in the original oil must be reduced to 7.5%, and the 28.9% of olein in the original

oil must be correspondingly increased by the hydrogenation to 69.5%, and this conversion of linolin to olein should produce a semi-solid product.

\* \* \*

But ordinarily in the batch process of hydrogenation, while the proportion of olein is being rapidly increased, there is also a small increase in the proportion of stearin. This is shown by the various samples produced by the defendant—particularly the series of samples L<sup>1</sup>, *et seq.*, terminating in (L<sub>6</sub>) and (L<sub>7</sub>), Exhibits A'13', which have the following composition:

	L <sub>6</sub>	L <sub>7</sub>
Per cent saturated glycerides	39.9	40.5
Per cent olein	56.2	55.6
Per cent linolin	3.9	3.9

In this case, starting with the original oil, the saturated glycerides have been increased from 23.3% to 39.9% in one case, and to 40.5% in the other.

The extent to which an oil or fat is saturated may be ascertained by finding how much iodine will be taken up by a given quantity of the oil or fat, for the iodine has the capacity of breaking the double bonds of the unsaturated glycerides and attaching itself thereto. If the fatty body will take up no iodine, it is said to have an "iodine value" of zero. Oleic acid has an iodine value of 90. Linolic acid has an iodine value of 180; i.e., by reason of its having two double bonds, linolic acid can take up twice as much iodine as oleic acid which has but one double bond. Cottonseed oil has an iodine value of 108 to 110, and the liquid fatty acids of cottonseed oil (i.e., the mixture of oleic acid and linolic acid after they have been separated from their glycerine molecules) have an iodine value of 147 or 148. Incidentally, one knowing the iodine value of the original oil or fat, and the iodine value of its liquid fatty acids, is able, by a simple mathematical formula, to ascertain the proportions of linolin, olein and saturated glycerides of such original oil or fat. One of the ways, therefore, in which an oil or fat is recognized, is by ascertaining its iodine value, as oils and fats have certain characteristic or identifying values.

\* \* \*

The various common oils and fats used for food or culinary purposes consist mainly, as already stated, of the glycerides of linolic and oleic acids and the glycerides of the saturated acids, palmitic and stearic, which are commonly grouped together and termed stearin.

There are traces of the glyceride of arachidic acid in cottonseed oil, but arachidic acid is a saturated acid and its glyceride is grouped with those of the other saturated acids under the term "stearin" or saturated fats.

The proportions in which these component glycerides are found in the various oils and fats differ. In lard, for example, we find 43% saturated glycerides, 8 to 10% linolin, and 48 to 50% olein, in olive oil, about 11% stearin, 8% linolin, and 81% olein.

\* \* \*

#### THE PRIOR ART

The catalytic hydrogenation of oils was first described by Dr. Wilhelm Normann in British patent No. 1515 of the year 1903 (Defendant's Ex. Book page

94) and in the corresponding German patent to LePrince & Siveke No. 141,029, Published May 4, 1903 (Ex. Book page 102). There is no corresponding United States patent, and the hydrogenation of oils in accordance with the Normann process and the products produced thereby are accordingly public property in this country.

Dr. Normann, in his patents, refers to the prior work of Sabatier and Senderens in hydrogenating various unsaturated hydro-carbons, and then states, beginning at line 27 of page 2.

I have found, that it is easy to convert by this catalytic method unsaturated fatty acids into saturated acids. . . . It is sufficient, however, to expose the fat or the fatty acid in a liquid condition to the action of hydrogen and the catalytic substance.

For instance, if fine nickel powder obtained by reduction in a current of hydrogen, is added to chemically pure oleic acid, then the latter heated over an oil bath, and a strong current of hydrogen is caused to pass through it for a sufficient length of time, the oleic acid may be completely converted into stearic acid.

The quantity of the nickel thus added and the temperature are immaterial and will only affect the duration of the process. Apart from the formation of small quantities of nickel soap, which may be easily decomposed by dilute mineral acids, the reaction passes off without any secondary reaction taking place. The same nickel may be used repeatedly. Instead of pure oleic acid, commercial fatty acids may be treated in the same manner. The yellowish fatty acids of tallow, which melt between 44 and 48° C. and whose iodine number is 35.1, will, after hydrogenation, melt between 56.5 and 59° C. while their iodine number will be 9.8 and their colour slightly lighter than before, and they will be very hard.

The same method is applicable not only to free fatty acids, but also to their glycerides occurring in nature, that is to say, to fats and oils. *Olive oils* will yield a hard *tallow-like* mass; linseed oil and fish oil will give similar results" (*Italics ours*).

\* \* \*

Normann describes his final product, produced by this progressive reaction from olive oil, as a hard "tallow-like" mass. Ordinary tallow, as Dr. Bacon points out, is of a somewhat semi-solid character, comparable with lard, and is one of the common cooking fats. Hence, Normann describes his final products by comparison with a common food fat, and Dr. Bacon has testified to the fact that,—

If an edible olive oil was started with, one would certainly obtain an edible hydrogenated product.

\* \* \*

Dr. Bacon has also testified that the Normann process is a commercial process which he has seen in use in this country on a commercial scale, and he is corroborated in this by Dr. Richardson. The underlying and pioneer nature of the Normann patent and process, upon which the world-wide industry of hydrogenized oils is based (whether these hydrogenized products be used for food, soap, candles, lubricants, or other purposes) has been emphasized by counsel for the plaintiff in his cross-examination of defendant's expert, Dr. Bacon.

Normann, in his patent, does not describe the purposes for which his hydrogenated fats are intended but leaves them to be inferred by those skilled in the oil and fat industry.

\* \* \*

Dr. Bacon has testified also that at the Larkin plant various degrees of hardness and of saturation are obtained in the commercial practice of the Normann process, and that these products, although edible, are nevertheless used for soap purposes.

\* \* \*

The brief then refers to Sabatier and Senderens work and to the Bedford thesis.

\* \* \*

Fokin, in his first publication of 1906 (J. Russ. Phys.-Chem. Soc. Vol., 38, pages 419-446), describes first, the hydrogenation of oleic acid and other fatty acids to various consistencies and degrees of incomplete hydrogenation. In experiment 28, he also describes the hydrogenation of almond oil and he states that after one hour he obtained a product of 30° titer (page 26 of translation, Ex. F). As the result of this experiment, with almond oil Fokin concludes:

Thus, the reaction proceeds with glycerides also.

In his second article of 1906 (ibid, Vol., 38, pages 755-758), Fokin further describes the hydrogenation of unsaturated fatty acids and glycerides, by carrying out the hydrogenation under pressure. With respect to the glycerides, he states:

The reduction of glycerides proceeds worse than that of free acids but nevertheless it is not difficult to convert linseed oil or any other drying oil whatever into substances with small iodine numbers, at first into products of the type of sunflower oil or poppy oil, and then into products analogous to sesame oil or cottonseed oil.

*Almond and olive oil undergo a metamorphosis into fats corresponding to beef or mutton drippings.*

Oils with large iodine numbers require a longer time, but at the final end they also give solid fats. (Italics ours).

Dr. Bacon points out that "beef and mutton drippings is what is known as beef tallow and mutton tallow; that is, the rendered fat of beef or mutton," and that such products are "very close to the lard range in melting point and actually used by many people for cooking and shortening purposes."

Dr. Bacon also points out that the iodine values of linseed oil, sunflower oil, and cottonseed oil, are respectively about 185, 120 and 110, so that when Fokin describes the conversion of linseed oil into products of the type of sunflower oil and then into products analogous to cottonseed oil, and finally into substances with small iodine values, he is describing a progressive reaction and degrees of hydrogenation far short of completion. T. R. 673. The above quotation from Fokin thus shows a clear appreciation by him of the gradual and progressive nature of the reaction, resulting in the gradual and progressive lowering of the iodine value, with the formation of various intermediate products which were comparable with natural products of like iodine values; and Fokin



clearly indicates that the various vegetable oils (including linseed, olive and almond) will give upon hydrogenation not only oils of lower iodine values but also solid and semisolid fats and products with small iodine values. Fokin thus describes clearly the production of intermediate products of all degrees of hydrogenation, from the original oil to the final hard fat, as a necessary and inevitable consequence of his process of hydrogenation.

In this second Fokin publication, Fokin also describes the hydrogenation of oleic acid to various degrees of saturation, and to products of various solidifying points, e.g., 54.5°, 46.5°, 32-24°, 61°, 45-44°, 64-62°.

In his third article, published in 1907, Defendant's Ex. Book, page 114 Fokin further describes the hydrogenation of oleic acid, croton oil and almond oil. In the case of oleic acid he describes several experiments which show the gradual and progressive nature of the reaction and the gradual and progressive conversion of oleic acid into a product of progressively increasing content of stearic acid, the actual percentage of stearic acid produced being stated after various time intervals.

In his fourth article, published in 1908 Ex. F, Fokin further describes the gradual and progressive nature of the hydrogenation of fatty acids and glycerides, giving many examples, and showing that the absorption of hydrogen is gradual and progressive. In fact, Fokin measured the progress of the reaction and found it to be of such a progressive nature that it is capable of representation graphically by plotting curves. These curves are found on pages 307 and 313 of the original Russian article (J. Russ. Phys-Chem. Soc. Vol., 40) and on page 1497 of the German article (Zeit. Angew. Chem. Vol., 22). In experiments, 16 and 17, of this fourth article, Fokin describes the hydrogenation of sunflower oil, also an edible oil and shows that it also undergoes a gradual and progressive hydrogenation, as indicated by the hydrogen absorption.

In their British patent No. 2520 of 1907, Bedford and Williams describe the catalytic hydrogenation of various organic substances, including fatty acids and their esters. They note that the hydrogenation of oleic acid results in the bleaching of the product, as well as its hydrogenation; and they point out that the product of their process is white and requires no further treatment (page 4, lines 13-16). With respect to linseed oil (a vegetable oil), they state—

Linseed oil is converted in a solid with solidifying point 53° C.

\* \* \*

On July 11, 1908, Paal & Roth published an article in the *Berichte der Deutschen Chemischen Gesellschaft* (Vol. 41, pages 2283-2291) in which they describe the hydrogenation of fatty acids and glycerides with the aid of colloidal palladium as a catalyst. Touching the reduction or hydrogenation of glycerides, they state Defendant's Ex. Book, pages 122, 123):

#### The Reduction of the Fats.

The animal and vegetable fats and oils are, as is well known, mixtures of the glycerine esters of saturated and unsaturated fatty acids; some of them contain in addition the glycerine esters unsaturated oxy-fatty acids. The ratio in which the glycerine esters are present in the separate fats is only relatively constant, it varies within certain limits. All fats without exception contain glycerides of unsaturated acids in the presence of glycerides of the saturated acids. The amount of glycerides of unsat-

urated acids is determined on the basis of the quantity of iodine or chlorine which they will take up.

The Hubl Iodine Number, which gives the quantity of iodine in percent of the amount of fat under certain definite conditions and which in food chemistry plays an important part in detecting adulteration and in the identification of the fats, is within certain limits, constant for each individual fat. According to the amount of glycerides of unsaturated acids contained in a fat the iodine numbers of different fat varies between 8 and 180%.

\* \* \*

The above-described transformation of oleic acid into stearic acid led us to expand our experiments to include the fats also. We chose as our starting material at first two vegetable fats, castor oil and olive oil, and an animal fat, cod liver oil, which have high iodine numbers and are therefore rich in unsaturated fatty acids. . . . By measuring the quantity of hydrogen absorbed and by determining the iodine number of the reduced fats, by the process usually employed in food chemistry, we could follow the progress of the hydrogenation and determine the end of the process. (*Italics ours.*)

Paal & Roth describe several experiments where they did in fact follow the progress of the reaction and noted the amounts of hydrogen absorbed at periodic intervals, the same as did Fokin in his 1908 publication. Paal & Roth started their hydrogenation at ordinary temperature, and followed it until the hydrogenation stopped, and they found it was necessary then to heat the reaction vessel to make the reaction continue. They explain this as follows:

An explanation of the effect of heating can be found in the fact that as the hydrogenation takes place, the product formed is solid at the ordinary temperature and separates out in the form of crystals which hinder the action of the colloidal palladium upon the oil. By heating, the crystals are liquefied and the hydrogenation again starts.

This explanation is in connection with the hydrogenation of olive oil, and not only does it show an appreciation of the gradual and progressive nature of the process, but it also shows that of necessity there was obtained by this reaction a semi-solid and incompletely hydrogenated product, solidifying at ordinary temperatures, but far from being completely hydrogenated; for even after heating and further hydrogenation they obtained from the olive oil a product still incompletely hydrogenated which softened at 43 and melted at 47. They state—

The iodine number of the hydrogenated fat was 9; this shows that the original oil had been hydrogenated to a considerable degree but that complete hydrogenation had not taken place by any means.

In their second article of May 8, 1909, in the same publication (Vol. 42, 1541 to 1553), Paal & Roth further describe their work, and state,—

Besides castor oil, and olive oil, which were studied in our first communication, we have experimented with the vegetable fats, croton oil, sesame oil, cottonseed oil, linseed oil, as well as animal fats as represented by butter, lard and oleomargarine. With these fats also it was rare that

we could at once accomplish a complete hydrogenation down to an iodine number of 0. But when the partially hydrogenated fats were subjected to another reduction, it was possible, in most cases, to accomplish complete hydrogenation.

In addition to thus emphasizing the progressive nature of the hydrogenation, and pointing out that products of greater, as well as of lesser, degrees of incomplete hydrogenation are possible, they note the improved properties of the hydrogenated fats, as to their rancidity,—

In contrast to the natural fats, which on standing naturally become rancid more or less rapidly, the hydrogenated fats show an extraordinary stability. After being kept for six months or a year in loosely stoppered bottles they remained entirely unchanged and had no rancid odor or taste.

With respect to croton oil, these authors note,—

The reduced fat had entirely lost the terrible burning taste of croton oil.

Not only did they thus taste the product, but they studied the physiological action of the partially and completely hydrogenated croton oil and found that the hydrogenation had converted the poisonous croton oil into a hydrogenated product which

when administered internally in a very large dose caused no diarrhœa or inflammation with a rabbit or with a dog,

and hence was non poisonous.

With olive oil, Paal & Roth repeated the hydrogenation, in the same progressive manner described in their 1908 article, carrying out the reaction in two stages. During the first stage the iodine value was reduced from 81 to 39.7 (about half way) and during the second stage from 39.7 to zero. The gradual and progressive nature of the process is emphasized by the fact that the complete hydrogenation required 29 hours time.

With sesame oil, Paal & Roth followed the progress of the hydrogenation by noting the hydrogen absorption at various time intervals.

Cottonseed oil was similarly hydrogenated, and with it, as with the other oils, the reaction progressed at ordinary temperatures until "the fat globules began to solidify out," whereupon the reaction vessel was warmed and the progress of the reaction continued. Thus with cottonseed oil, as with olive oil, Paal & Roth describe the production of incompletely hydrogenated products solidifying at ordinary temperatures.

Paal & Roth note also that the hydrogenated cottonseed oil fails to respond to the Halphen test.

They also hydrogenated butter, lard and oleomargarine, three of the best known food fats. The hydrogenized butter had "a slight pleasant nut-like taste" and "after standing nine months there was no sign of any change in the product." Another hydrogenated butter had a melting point of 39.5–41 and an iodine value of 13.6, and it was therefore a semi-solid and incompletely hydrogenated.

Paal & Roth thus hydrogenated most of the common oils and fats used for food purposes. They noted the freedom from rancid taste and odor of the hydrogenated fats even after long standing. Only in the case of the poisonous

croton oil did they consider it necessary to make a direct statement of their physiological tests (made in the usual manner in which such tests are commonly made to ascertain whether a product is poisonous or edible) and in this case they observed that the hydrogenated product was no longer poisonous but was rendered innocuous by the hydrogenation. They also called attention to the absence of "the terrible burning taste of croton oil" in the hydrogenated product.

\* \* \*

Erdmann, in his German patent No. 211,669 of 1907 (published July 13, 1909). Defendant's Ex. Book, page 105, describes, in Example 3, the hydrogenation of a low melting tallow of solidification point 31° into a harder tallow of solidification point 38°, which, as Dr. Bacon points out, is a product "still very far short of complete hydrogenation." Completely hydrogenated tallow would have a solidification point of about 55 or 60°. Tallow, as pointed out by Dr. Bacon, is one of the common food fats.

#### KAYSER

Edwin Cuno Kayser is the patentee of U. S. patents No. 1,004,035, granted September 26, 1911, on an application filed March 20, 1908, and No. 1,008,474, granted November 14, 1911, on an application filed Feb. 18, 1910. Both patents were granted to The Procter and Gamble Company (the present plaintiff) as assignee and have since been transferred to the Hydrogenation Company. Q258-262, D. R., page 35. The applications for these patents were prosecuted before the Patent Office by the same attorneys who prosecuted the application of the Burchenal patent in suit, as appears from the file wrappers in evidence, Ex. G and H, and both applications were filed long before the filing of the application for the Burchenal patent in suit. These Kayser patents will expire some four years prior to the expiration of the Burchenal patent in suit, and the right to practice the processes of these patents and to produce the products of such processes will then become public property.

Burchenal has testified that the Kayser applications were filed with his knowledge and approval, and he has expressly disclaimed inventorship of any of the processes or parts thereof described in the specifications of these two Kayser patents.

\* \* \*

Kayser came to this country in November of 1907, and went immediately to Cincinnati, where he began negotiations with the Procter & Gamble Company, through their General Manager Burchenal, to interest the Procter & Gamble Company in a process which he had manipulated for some three years; a process which he said he alone was thoroughly familiar with, and which was "of the greatest possible importance to soap manufacturers," the Procter & Gamble Co. being then soap manufacturers. It appears that Kayser began his work on the catalytic hydrogenation of oils in 1904, a year or so after the publication of the Normann British and German patents in 1903, and that Kayser's work, before coming to this country, was at Joseph Crosfield & Sons, Limited, of Warrington, England. D. R. 11, Q57-59; 28, Q191; 64, Q449, 207; and 211, Q9. Crosfields were naturally much put out about Kayser leaving them and coming to this country, D. R., 154, Q164, since, as Kayser states in his letter of October 18th, he alone was thoroughly acquainted with the manipulation of the process which

he had been using for three years and which he proposed to introduce in this country as a process "of the greatest possible importance."

As was to be expected, under the circumstances, Kayser brought with him samples of the products which he had been producing at Crosfield's, and it was these products which he showed to Burchenal. At least one of these products was produced by hydrogenation from cottonseed oil. D. R., 9-10, 39. Burchenal had no knowledge or interest in hydrogenation prior to this time. D. R., 227-228. It is Burchenal's assertion that the products Kayser brought with him were very hard, but the only written record of any of these products is of a product "which showed an iodine value of 52.26 and a melting point of 39.3° C." D. R., 122, last paragraph. It is indeed significant that the only record of any product which Kayser brought to this country from Crosfield's in England had a melting point of 39.3° C. and an iodine value of 52.26. This product, which Kayser showed to Burchenal, had a melting point within the range of melting points given in the specification as filed of the Burchenal patent in suit, and within the range now given in the patent in suit. The iodine value of said product is less than 3° lower than the lower limit of iodine values of the Burchenal patent in suit, and far closer than is the iodine value of the defendant's product Kream Krisp to the upper limit of iodine values of the patent in suit. If one may then judge from the report of Dr. Bender, Procter & Gamble's chemist at the time, and from the records of Procter and Gamble, the only samples from Crosfield's which Kayser brought to this country are the samples having a melting point and iodine value which correspond to those of the Burchenal patent in suit. It is evident that Burchenal cannot claim that he is the inventor of any hydrogenized oil or fat such as that which Kayser brought to this country and showed to him.

After the preliminary negotiations and the building of a small plant for his process at the plant of Procter and Gamble in Cincinnati, Kayser gave a demonstration of his process which is described in certain notes or reports which are reproduced at pages 120-124 of the deposition record. These notes describe the Kayser process in detail, as it was disclosed by Kayser to Burchenal and to Anderson, and as it was practiced and demonstrated by him. The process is in all essentials identical with that described in the Kayser patents Nos. 1,004,035 and 1,008,474 above referred to. In demonstrating his process Kayser produced products of varying degrees of hardness, as indicated by the following melting-points: 55.5° C.; 60.3° C.; 55° C.; 60° C.; 42° C.; 43° C.; 59.8° C.

The apparatus which was built for Kayser, and in which he demonstrated his process to Burchenal, was completed and operated in January, 1908. D. R., 11 Q61; 122, Q851. Burchenal was quite familiar with the apparatus at the time and observed its operation at various times in the early part of 1908. D. R. 90, Q601-604, and he was also familiar with the reports made by Kayser to Anderson:

Q385. And reports were made by Mr. Kayser to Mr. Anderson?

A. Yes, sir.

Q386. And it was from Mr. Anderson that you obtained your knowledge of the reports? A. Oh, no; I was in touch with them daily.

Burchenal thus knew everything that Kayser was doing; and in particular he knew of the reports of Kayser, with which he was in contact daily. These reports, which are in evidence, are few in number. One of them, that of March

5, 1908, describes the hydrogenation of cottonseed oil, to given products with a melting point of 42° C. and 43° C., respectively. D. R., 124, 125, Q853. Anderson, to whom these reports were made, has testified that these reports were absolutely true at the time they were made, D. R., 170, Q100, and that Kayser was left absolutely to his own initiative in the carrying out of his process and every facility provided him.

\* \* \*

The Kayser process, as described in Kayser's reports, and in the Kayser patents, has been demonstrated by defendant's witness Richter in the presence of counsel and experts for the plaintiff. The catalyzer was conceded to have been produced in accordance with the process used by Kayser, T. R., 591, and the apparatus and conditions of operation used were those of the Kayser reports and the Kayser patents. These experiments are described by Richter, and the propriety of the procedure or the apparatus was not questioned on cross examination. The oil used was refined cottonseed oil, the same as Kayser used in the demonstration of his process to Burchenal early in 1908. The reaction was noted as being a gradual and progressive reaction and the oil was gradually increased in hardness as the reaction proceeded. T. R., 608, Qs225-226. This was in fact to be expected from the very nature of the process, which involves the bringing of films or a spray of the oil and catalyst progressively into an overlying body of hydrogen in order that the necessary contact between the hydrogen, catalyst and oil may take place and in order that the reaction may proceed. Samples were taken from time to time during the progress of the process and these samples which have been produced in evidence show clearly the gradual and progressive nature of the reaction. As with the series of samples produced by Dr. Walker, Ex. M, so the series of samples produced by Richter by the Kayser process show a gradual and progressive hardening or saturation and a gradually increasing melting point. The two experiments demonstrating the Kayser process were called respectively the "K-run" and the "L-run." The series of samples are marked respectively: K-0, K-1, K-2, &c., and L-0, L-1, L-2, &c. The L-run was for the purpose of producing the products of melting point of 42° C. and 43° C., respectively, which Kayser produced and showed to Burchenal on March 5, 1908. These various samples and their melting points, as well as the time required for their production, are shown in the following table:

K- AND L-RUNS (KAYSER PROCESS).

No. of Sample.	Time.	Melting Point.	
K-0	0	liquid (cottonseed oil)	
K-1	17 min.	liquid	
K-2	27 "	liquid	
K-3	37 "	90.5° F.	32.5° C.
K-4	42 "	92.5	33.6
K-5	57 "	95.4	35.2
K-6	72 "	101.2	38.4
K-7	77 "	100.5	38.
K-8	123 "	106.	41.1
K-9	303 "	115.8	52.3
K-10	480 "	121.0	46.5
K-11	715 "	126.2	49.4

No. of Sample.	Time.	Melting Point.	
		liquid (cottonseed oil)	
L-0	0	liquid	
L-1	1 hr.	liquid	
L-2	2 "	97.5	36.4° C.
L-3	3 "	103.0	39.4
L-4	3½ "	106.0	41.2
L-5	3¼ "	106.8	41.8
L-6	3 hr. 50 min.	107.8	42.1
L-7	4 hr. 5 min.	108.9	42.8

\* \* \*

The products designated L-6 and L-7 are the products which correspond, within a small fraction of a degree, to the products of melting point 42° C. and 43° C., which Kayser produced and showed to Burchenal on March 5, 1908, D. R., 124, as above pointed out. The iodine values of these two products L-6 and L-7 are respectively 55.4 and 54.5, which correspond to the iodine value 55 found as the lower limit of iodine values in the Burchenal patent in suit. These two products L-6 and L-7 therefore have the same melting points and iodine values as the product of the patent in suit, as such product was defined in the application when filed, since this application as filed gave no other directions for producing the product than to stop when the product had a melting point of 36 to 43° C.; and such products were stated to have an iodine value of 55 to 80. Nevertheless, and even though these samples L-6 and L-7 correspond in melting point and iodine value with the products of the Burchenal application as filed, their composition, as indicated by their content of saturated glycerides, olein and linolin, is quite different from that introduced into the Burchenal application by amendment and now found in the Burchenal patent, as will appear from the following comparison.

*Burchenal Patent*

		L-6.	L-7.
Melting point (application as filed).....	36-43	42.1	43.1
Iodine value.....	55-80	55.4	54.5
Saturated glycerides.....	20-25%	39.9	40.5
Olein.....	65-75%	56.2	55.6
Linolin.....	5-10%	3.9	3.9

The composition of these two products, L-6 and L-7, is shown on triangular chart 403. D. R., 609. It may be here noted, as is pointed out elsewhere in the brief, that the Kayser process followed in producing these products L-6 and L-7 is the same process described in the Burchenal patent in suit, and that the Burchenal patent gives no other directions for the production of a product having the composition specified in the patent than those which were followed in the production of L-6 and L-7. The semi-solid product of the patent, therefore, cannot be produced without experimentation and without ascertaining the necessary conditions for its production; and the product having the composition stated in the patent is not accordingly the product originally described and having the melting point and iodine value originally stated.

The samples L-6 and L-7 are edible, T. R. 592, Q134; 611, XQ259; and Richter has testified that he has made many products by the same process and

of a similar nature and that they all proved edible. T. R. 611, XQ263. Upon aeration of these products L-6 and L-7, by laboratory methods, to approximate those in which lard and lard substitutes are aerated by passing over the chilling rolls and aerating with pickers, these products are converted into a "salve-like product" of lard consistency as appears from Exhibits C-1 and D-1, and from Richter's testimony.

The product L-3 has a melting point of 39.4, which is almost identical with the product of melting point 39.3 which Kayser brought to this country from Crosfield's and showed to Burchenal. This product is even softer in consistency than the samples L-6 and L-7, as is to be expected from its lower melting point. The samples K-6 and K-7 are also of a like melting point to that of the product which Kayser brought to this country and showed to Burchenal as one of the products (and the only product so far as the records of Procter and Gamble show) of the process which he desired to exploit in this country and which he represented to Procter and Gamble as a process as "of the greatest possible importance."

The history of hydrogenation at Procter and Gamble's will be dealt with more in detail in a subsequent portion of the brief; and it will be shown that edible hydrogenized cottonseed oil was used in making lard substitutes and that such lard substitutes were sold in large quantities by Procter and Gamble long before the alleged invention by Burchenal of the food product of the patent in suit; so that such lard substitutes are also a part of the prior art so far as the Burchenal patent in suit is concerned. In the present discussion of the Kayser process, as a part of the prior art, we have shown that the Kayser process, as well as the batch processes of Normann, Fokin, and Paal and Roth, is a gradual and progressive process and a process which inevitably and of necessity gives all the intermediate products between the original oil and the final and ultimate degree of saturation which may be aimed at. We have also shown, by producing the products which Kayser brought to this country and showed to Burchenal, and which Kayser produced on March 5, 1908, and showed to Burchenal, that they were edible products, as Burchenal in fact concedes, and that these products correspond to the product of the Burchenal application, as filed, of the patent in suit. In Kayser's actual demonstration of the process in 1908, as Burchenal has testified, samples were taken from time to time, just as samples were taken from time to time in the K- and L-runs above referred to. Burchenal in fact states that the taking of samples from time to time was the regular procedure in experimental work. D. R. 17, Qs100-101. Burchenal also appreciated that the Kayser process was a progressive reaction during which the hydrogen was gradually absorbed, the oil gradually hardened, the iodine value gradually decreased, and the solidification point gradually raised. D. R. 21, Qs133-136. Anderson has similarly testified that the Kayser process is a gradual process and a progressive reaction, the oil gradually changing from a liquid to a semi-liquid consistency and then to a relatively hard consistency.

\* \* \*

Kayser had been manipulating his process for three years before he came to this country and he himself stated in his letter, D. R., page 207, that he was thoroughly familiar with it. He brought to this country samples of a melting point of 39.3° as representing the products produced by his process; and on the basis of these samples, and perhaps others of which there is no analytical record,



he induced Procter and Gamble to sidetrack other work in order to give him the right of way to demonstrate his process by which such products could be produced.

\* \* \*

The only oil particularly referred to in the Kayser patents is cottonseed oil; and the evidence shows that this is the only oil that he hydrogenized in his early work in this country, as well as one of the oils which he hydrogenized and brought to this country with him. It was moreover refined cottonseed oil that Kayser used in all his work after coming to this country in 1908. D. R., 167, Qs69-73.

\* \* \*

Kayser finally concluded his work in this country and returned to England. He is now a stockholder in the Procter and Gamble Company. D. R., 51, Q376. The defendant in this case, misled into believing that Kayser was no longer in the employ of the Procter and Gamble Company or subject to its control, T. R., 639, went to great expense and trouble in an attempt to find Kayser and find out from him about his work in this country; and a representative was sent to England in war time to interview Kayser, only to find, after long delay and much difficulty, that Kayser's mouth was closed. We now know that Kayser has been in the employ of Procter and Gamble continually and that he is under agreement with them not to disclose any information regarding anything he did while in their employ. Similarly an attempt was made to find out from Crosfields about the work which Kayser did before coming to this country. But Crosfields' mouth was also closed. We now know that the relations of Crosfields with the Procter and Gamble Company are such that, in the language of Burchenal:

We would consider it a breach of faith if they (Crosfields) disclosed any information regarding the hydrogenation of fats, to the competitors of the Procter and Gamble Company.

The only information, therefore, which we have about Kayser's work in this country and his relations with Burchenal, is the oral testimony of officials of the plaintiff company and the reports of Kayser's work which are in evidence; and the testimony of Kayser's friend and only confidant, Clarence von Phul.

After Kayser had completed his work in this country and had returned to Europe; after he had demonstrated his process, had produced his products, and had made his final contract; after he had been made a stockholder in the Procter and Gamble Company; and after Crosfield had in 1909 been paid a large sum of money for their rights in this country, D. R., 153-155, Kayser left this country in July of 1910. D. R., 116; Q818. After Kayser was thus out of the way, and had been placed under contract not to disclose anything he did in this country; then, and only then, did Burchenal, in November, 1910, file the application of the patent in suit and claim the semi-solid product of Kayser's process as his (Burchenal's) invention.

It will possibly be urged on behalf of plaintiff that the semi-solid products which Kayser made on March 5, 1908, of a melting point of 42 and 43° C., were not produced intentionally and were not considered to have any value. But such a contention is of no persuasive force, inasmuch as among the products which Kayser brought with him to this country and showed to Burchenal, was

one shown by Procter and Gamble's own records as having a melting point of 39.3° C., exhibited by him, with the others, as products produced by his process, which he had represented as "of the greatest possible importance." In respect of the products of a melting point of 42 and 43° C., produced by Kayser on March 5, 1908, these products were produced by Kayser and shown to Burchenal and Anderson, and Anderson's report describing these products and their melting points was considered of such value that it was kept as one of the very few reports of the work which Kayser did.

\* \* \*

#### PLAINTIFF'S CONTENTION AS TO PRIOR ART UNTENABLE

##### 1. *Utility.*

Dr. Baskerville contends that any product of a degree of hydrogenation short of substantial completion is not described or suggested in the prior art as having any utility whatsoever. T. R., page 758, Q190. He does not contend that the completely hydrogenated products were not recognized as having utility. He assumes on the contrary that these products were for use in making soap or candles. T. R., page 750, Q182. If he concedes that oil technologists, or those skilled in the fat and oil industry, had sufficient information to employ the hydrogenated products in the manufacture of soap and candles by exercising the skill of their calling, he is illogical in not further conceding that in the exercise of that same skill they recognized the utility of the hydrogenated fats in the production of food products.

But it cannot be of importance whether the investigators of the prior art actually described, or even knew of, all the uses to which their products could be put, for, as a matter of law, they are entitled to all the uses thereof whether they described or conceived of such use or not, as has uniformly been held by the courts.

\* \* \*

It follows, as a conclusion of law, that Normann, Fokin, Bedford and Williams, Paal and Roth, Erdmann and Kayser, were entitled to use their respective products, in any of the various degrees of hydrogenation in which they might be produced, for any of the uses for which they were adapted, whether they described or conceived of all of such uses or not.

And just as inventors are entitled to all the uses of their inventions whether they had conceived of or described such uses or not, so the public is entitled to all the uses of things which are public property.

\* \* \*

It logically follows that Burchenal could not patent the old hydrogenized fats of the prior art, as food products, merely because he was the first to describe their use for that purpose; for, under the decisions above cited, the new use of and old thing does not make the thing itself patentable, even if such use had not been proposed before. And this would be true even if the old products were not known to be edible, or were even considered inedible.

\* \* \*

The hydrogenized products of the prior art are, in fact, edible, and this is not denied, but conceded.

\* \* \*

And yet Dr. Baskerville stakes the plaintiff's whole case upon the alleged discovery

that the partially hydrogenated oil itself could be used directly as a food.  
T. R., 757.

## II. Degree of Hydrogenation or Saturation.

Dr. Baskerville contends that the aim and object of the investigators of the prior art was complete saturation; that the idea of partial saturation seems to him to have been incidental; and that the stopping of the process to give a semi-solid product was not taught in the prior art. T. R., 758. Yet the processes of Normann, Fokin, Paal and Roth and Kayser, were all of a gradual and progressive nature, and were so recognized and described; and, as a necessary step in carrying out such processes, all the various intermediate degrees of partial hydrogenation were obtained. Fokin, Paal and Roth and Kayser all point out how the reaction can be followed step by step, and Kayser specifically states that semi-solid products are obtained if desired. Dr. Baskerville cannot, in the face of these prior disclosures, be heard to deny that semi-solid and incompletely hydrogenized oils of different consistencies were, in fact, produced and described. Apparently Dr. Baskerville did not know that the product Kayser brought to this country and showed to Burchenal as the product of a process "of the greatest possible importance" was a semi-solid of melting point 39.3° C. and iodine value 52.26, and he did not recall the teaching of the Kayser patents.

\* \* \*

That it is an obvious thing to stop the hydrogenation half way, or at any other intermediate point, instead of carrying it to completion, and that anyone would naturally know, and as a matter of course did know, that this could be done, without knowledge of the patent in suit, and without invention, is indicated (in addition to Kayser's disclosures) by the following excerpt from the British patent to Paal No. 5188 of 1911, which counsel for plaintiff was the first to quote as interpretive of the prior art and which was published long prior to the grant of the patent in suit.

The reduction process may also, *of course*, be carried on in such a manner that only partial reduction ensues. These partially reduced fats then exhibit a lowered melting point and a consistency resembling ointment.

The degree of hydrogenation can be determined by ascertaining the iodine value. (*Italics ours.*)

\* \* \*

An unprejudiced view of the hydrogenation of oils for food purposes is found in Bulletin 469 of the Dept. of Agriculture, entitled "Fats and Their Economic Use in the Home" by Holmes and Lang, Scientific Assistants, Office of Home Economics, published Dec. 15, 1916. This Government publication was first quoted by Dr. Baskerville as an authority, T. R., 746, and was introduced in evidence by the defendant as Exhibit P2. Defendant's Ex. Book, pages 151-177.

The following is found on pages 14 and 15. Ex. Book, pages 164-165.

Hardened vegetable oils, technically known as hydrogenated oils, which have much the same consistency as lard or butter, have been put on the

market within recent years. They are commercial possibilities owing to the fact that as a result of a long series of laboratory experiments, processes have been discovered by which oils may be transformed into a product of any desired hardness by chemically adding hydrogen to them. This reaction takes place, for instance, when finely-divided nickel hydrogen and the oil to be hardened are intimately mixed under proper conditions. The nickel does not enter into the composition of the hardened fat, but is removed and used repeatedly in the preparation of other batches. The hardened oils are generally white in color, have no appreciable odor or taste, and are less likely to become rancid than the original oil. (Italics ours.)

Burchenal made no "laboratory experiments" and "discovered" no "processes" which resulted in such "commercial possibilities." Normann, Fokin, Bedford, Paal and Roth made the experiments and discovered the processes, and published these to the world. Burchenal has done nothing to "advance the progress of science and of the useful arts" that would entitle him to take away from these prior experimenters and discoverers the fruits of their labors, and from the public its birthright. Yet to permit his patent to stand would be to deny Normann and the other prior investigators and patentees the right to put to the chief use of fats—that as food—their hydrogenated products, in the various degrees of saturation which they describe.

\* \* \*

### III. Use of Hydrogenized Fats for Food.

Dr. Baskerville argues that the teaching of the prior art repels rather than suggests the use of hydrogenized oil for culinary purposes. In support of his contention, he gives his reasons which may be briefly condensed and discussed as follows:

1. He suggests, by inference, that the hydrogenized oils were to be used for candles and soaps. Q182, T. R., p. 750. Why he picked out these two products to the exclusion of food products is not apparent, because the prior art patents and publications describe specifically no special uses for the hydrogenized products. It would have been as superfluous for the earlier patentees and investigators of hydrogenized fats to suggest the common and ordinary uses of the fats, as it would have been for the originator of aniline by a new process to say it could be used for dyes, or of the originator of synthetic sugar to say that it could be used as a sweetening for food. And it is conceded by Dr. Baskerville, and by counsel for plaintiff, as it must be conceded, that the products of the prior art were in fact edible, whatever their degree of hydrogenation. T. R., 676.

2. He says that Normann's statement in his British patent No. 1515 of 1903 that there were no secondary reactions in hydrogenation "apart from the formation of small quantities of nickel soap which may be easily removed by dilute mineral acids" indicates that the product is something which is not to be regarded as suitable for food.

Dr. Bacon has logically pointed out that Normann told how to remove those nickel soaps which might have prevented such use, thus indicating to any skilled chemist, in terms which a chemist would understand, that the product was edible.

\* \* \*

3. Dr. Baskerville quoted Paal and Roth, who had discovered in the course of their physiological investigations that hydrogenation changed an inedible or poisonous croton oil into an edible or non-poisonous tallow. To anybody but Dr. Baskerville, this would indicate that Paal and Roth, by their physiological investigations, *of course knew* that the usual food oils were edible when hydrogenized, and commented only on what was really a discovery, to wit, that poisonous croton oil became non-poisonous on hydrogenation. He quoted their statement that they studied the *partially* and completely hydrogenized oil, and their statement that cottonseed oil when hydrogenized gave a negative Halphen test. The several quotations Dr. Baskerville gave from Paal and Roth's article show that they said they employed the tests "*used in food chemistry.*" It seems to us that the significance of that statement has entirely escaped Dr. Baskerville as well as their statement that they studied the *partially* hydrogenized oil.

\* \* \*

5. He summarizes his conclusions as follows:

So it appears to me that Burchenal really made a seedless prune, as you may put it, or spineless cactus. He Burbanked the oils, as you might put it. And by his *work* he actually made two discoveries: first, that the hydrogenated oil could be put into a compound and used as a food; and, second, that the partially hydrogenized oil itself could be used directly as a food, and thus he founded what is known as the hydrogenized food industry. (*Italics ours.*)

\* \* \*

Burchenal says that neither he nor anyone on his behalf made any tests of hydrogenized oils for cooking or edible purposes before Flake White containing hydrogenized fat was put on the market and sold. On the contrary, Burchenal claims that he merely used his perceptive faculties, or, as he put it, arrived at a conclusion that Kayser's hydrogenized oil was edible—by a process of "cerebration." But even if one should have made some experiments to see whether the hydrogenized fats were edible, would that have required the exercise of the inventive faculty? Dr. Baskerville says, in effect, that it would have been the normal every day work of a food or oil chemist, for first he concedes that the greatest use of fats and oils of animal and vegetable origin is for foods, and then he concedes that if an oil or fat unknown to him had been presented to him, he would have used the expected skill of his calling and ascertained its technological uses by casting "around to see the uses that fats were put to." T. R., 772; XQ282-286. Probably he would not have been so sapient as Burchenal claims to have been in arriving at a conclusion that hydrogenized fats were edible, merely by a process of cerebration, and would have eaten some of the fat or cooked with it, but that would have been only the ordinary use to which fats are put. Yet surely this cannot be considered an exercise of the inventive faculties.

\* \* \*

Dr. Baskerville would have cast about to see what use fats were put to. Can he imagine that Normann, or Fokin, or Paal and Roth did not do that? They were scientific men. They did not state the obvious. Paal and Roth ~~announced what~~ was not obvious, to wit, that poisonous croton oil was ren-

dered non-poisonous; and if they had thought that edible oils when hydrogenized were rendered inedible or poisonous, it is unthinkable that they would not have said so.

It is apparent then that Dr. Baskerville's conclusions are untenable. Burchenal's Burbanked "seedless prune" and "spineless cactus" on closer inspection are found after all to be only plants of the common garden variety.

Dr. Baskerville paid his tribute to the wrong person. It was Normann who "Burbanked the oils."

\* \* \*

*From whatever aspect this case be viewed, when the discovery that oils and fats may be hydrogenized into solids or semi-solids (and thereby be availed of in such form as lard substitutes) is considered, it is to Normann "that the honor of this discovery belongs." It does not belong to this country or to Burchenal.*

#### FURTHER DETAILS OF EARLY HYDROGENATION WORK AT PROCTER & GAMBLE'S

Reference has already been made herein to the Kayser patents 1,004,035 and 1,008,474, which were cited as references by the Examiner against the claims of the patent in suit, and which are admitted by Burchenal as part of the prior art.

The defendant, under order of the Court, took the depositions of Burchenal, Anderson, McCaw and Morrison, all officers of the plaintiff company, in reference to the Kayser process of hydrogenizing oils.

The following facts, briefly hereinbefore referred to, were developed:

Edwin Cuno Kayser had for some years been in the employ of Crosfield & Sons, Ltd., an English firm, which with Dr. Normann, D. R., page 76, Q518, had been developing improved procedures in the hydrogenation of oils. On October 18th, 1907, Kayser wrote to the plaintiff, whose main business was then and is now the manufacture of soap, stating that he proposed visiting the United States for the purpose of introducing "a process of the greatest possible importance to soap manufacturers," that he had manipulated the process for three years, and was "the only person thoroughly acquainted therewith."

After a brief correspondence, Kayser arrived in this country in November, 1907, and called on Burchenal, bringing with him samples of hydrogenized oils including hydrogenized cottonseed oil and hydrogenized maize (corn) oil and showed them to Burchenal. Burchenal had never before seen or heard of hydrogenized oils, and was not even familiar with lard compounds. The samples brought by Kayser were "very light in color, pale yellow or almost white." After certain negotiations, a preliminary contract was made with Kayser on Dec. 5, 1907, and Kayser then told Burchenal that the samples referred to had been produced by hydrogenating cotton seed oil in the presence of a catalyst.

Kayser was very secretive and mysterious and evidently disinclined to tell anything more than he had to. Burchenal says "There was a good deal of mystery about Mr. Kayser." There is, however, a written record giving a qualitative analysis of one of Kayser's samples brought from Crosfield & Sons, showing that it was a semi-solid, with "an iodine value of 52.26 and a melting point of 39.3° C.," so that the first hydrogenized oil which Burchenal ever saw was a "white or yellowish semi-solid" with a melting point within the range of 36°-43°, the range which Burchenal specified, when he filed his application for the patent in suit, as the melting point range of his product and within the melting point range of 33 to 40° specified in the patent itself.

Burchenal says now that Kayser's samples were hard, but the report is clear as to the melting point, and is more to be relied on than Burchenal's assertion or memory.

Burchenal was *forced*—unwillingly it is true, *to concede that those samples which Kayser had brought from England were edible.*

Q393. But was there anything inherent to this product which he brought with him, which rendered it inedible?

A. *Nothing*, I should think, except the fact that the idea of edibility had not been associated with it. (*Italics ours.*)

During December, 1907, and the early part of January, 1908, a small experimental plant was built under Kayser's directions at the plaintiff's factory, including a hydrogenating apparatus like that shown on sheet 1 of the drawings of the Kayser patent 1,004,035, and capable of hydrogenizing a batch of 20 pounds of oil. D. R., pages 160-165. The process and the apparatus were disclosed in detail to Burchenal and Anderson, and also the precise method of making the nickel-kieselguhr catalyst. On January 17th, 1908, Kayser alone hydrogenized refined summer yellow cotton-seed oil in his apparatus and produced hardened fats of melting points of 55.5° C. and 60.3° C. D. R., 122-123. Five days later on January 22, 1908, in the presence of Anderson, Kayser hydrogenized a second batch of the same oil, and during the month of January, 1908, there was prepared by Anderson, under Kayser's directions, a complete description of the process of hydrogenation, which appears on pages 120 and 121 of the Deposition Record, and which contains the following:

The process of saturation is very interesting. Hydrogen is circulated as taken up by the fat. . . . The affinity of the fat for the hydrogen is plainly evidenced in this operation. As the saturation nears completion, less gas is, of course, taken up by fat and an excess is circulated, which causes bubbling at end of the outlet tube. Completion of saturation is indicated by comparison of volume of gas in and out of machine. When saturation is practically complete, the gas passes through without any apparent reduction in volume. The fat is drawn out of the machine—a black mass, on account of presence of catalyzer, and passes through filter press, the catalyzer filtering out very rapidly. The filtered fat is the finished product.

There were in addition three other written reports, dated respectively Feb. 6, 1908, March 5, 1908, and May 7, 1908, all printed in the Deposition Record on page 124, showing work done by Kayser in the hydrogenation or treatment of oil. The first shows a mixture of hydrogenized oil and "prime tallow"; the second, two batches of semi-solid hydrogenized oil, *one having a melting point of 42° C. and the other having a melting point of 43° C.*; and the third showing the melting point of the fat acids of a large batch of hydrogenized oil sent to McCaw at Macon, Ga. (These fats of 42° and 43° C. melting point have been reproduced by Richter as Exhibits A' and A' and have already been discussed.)

Anderson says that the cottonseed oils treated by Kayser were all "*refined oils*," Q74, D. R., page 167, and therefore edible. Burchenal and Anderson were in daily touch with the work Kayser was doing—but all the other employees of the plaintiff were kept in ignorance. On this point Anderson testified as follow (*italics ours*):

Q326. Who besides Mr. Burchenal, Mr. Kayser and yourself saw or became familiar with any of the processes or products carried on or produced by Mr. Kayser during 1908 and 1909? A. Well, during 1908, no one but Mr. Burchenal and myself. We occasionally gave Mr. Kayser a laborer to help him, but we changed the laborer every week. *He did all the work himself* and no one came in contact with him but Mr. Burchenal and myself.

Q327. How about 1909? A. 1909, after we started the plant, Mr. Leach was introduced into it.

Q328. Since that time the process— A. And it has gradually broadened out since that time. *In the first two years we would arrest anyone—anybody who was seen talking to Kayser, except ourselves.*

Q329. That same degree of secrecy has practically been preserved ever since? A. Oh, no; it has broadened quite a lot beyond that—quite a few people now know about it.

Q330. Quite a few people know it, in order to carry on the process? A. In order to carry on the large volume of business, to take care of the increased work.

Q331. But the knowledge is confined to such people as you employ? A. Yes.

Q332. The knowledge is confined to such people as you employ in making the hardened oil or substance? A. In the beginning our laboratory people did not know anything about it, as such.

Q333. And you, up to the present time, keep the knowledge from the public just as far as it is possible to do so? A. *Just as far as we know how.*

Anderson was asked whether the products produced by Kayser on March 5, 1908, having melting points of 42° and 43° C. *were edible as food products and he stated that they were.*

Q235. And would you also say that a product having a melting point of 42 degrees Centigrade and produced by circulating hydrogen gas through cotton-seed oil, in which nickelized kieselguhr is maintained in suspension by agitators in the presence of hydrogen gas, under pressure, the oil being heated to a temperature of 160 degrees Centigrade, would produce a commercial lard substitute? A. Yes.

\* \* \* \* \*

Q265. Is it your opinion that a product having a melting point of, say, for example, 42 degrees Centigrade, and produced by treating cotton-seed oil with hydrogen in the presence of an atmosphere of compressed hydrogen, and in the presence of nickel deposited upon kieselguhr, and maintained in suspension in the oil by agitation, the oil being heated to a temperature of 155 degrees or 160 degrees Centigrade, and without being subjected to treatment to remove the characteristic taste and odor due to hydrogenation, would be commercially acceptable as a fat for use in frying, or as a fat for use in shortening dough?

Mr. Allen: The question is objected to as incompetent, indefinite and misleading; also as irrelevant and immaterial.

A. Why, I would consider such a product entirely edible; but to be a commercial success, it would be preferable to subject the product to the



treatment to which lard and other cooking fats are regularly subjected or usually subjected.

Burchenal states that the process practiced by Kayser is the same process described in Kayser's patent 1,008,474, and is the same described in the patent in suit, as follows:

Q754. Referring now to Questions 264 and 265, is the process described in the Kayser patent 1,008,474 materially different from the process practiced by Mr. Kayser in the early part of 1908? A. As I understand the patent, it is not materially different.

Q755. That is, the process which is described by Mr. Kayser in this patent is not materially different from the process which he practiced in the early part of 1908 at the Procter & Gamble Company's factory? A. Yes.

Q756. Referring now to Question 334, is there any difference in the process of hydrogenation described in the patent in suit and the process which was carried out by Mr. Kayser in the early part of 1908? A. As I understand that paragraph, it does not refer to any special process, except where it says "preferably"; but preference was given to the process in a general way as outlined in the Kayser patent.

Q757. That is, so far as the process is described in the patent in suit, it is the same process which Mr. Kayser had carried on in the early part of 1908 in the hydrogenation of oils, and particularly cotton-seed oil? A. The process of hydrogenating, yes.

Q758. And your knowledge of this process was gained from Mr. Kayser? A. Yes.

\* \* \*

From January to May, 1908, Kayser made quite a large amount of hydrogenized refined cotton seed oil by his process and apparatus and in May of that year some 450 pounds thereof was sent by Mr. Procter to the McCaw Mfg. Co., at Macon, Georgia, to have it made up into lard compound by substituting it for the usual oleo stearine. At that time the McCaw concern, of which W. E. McCaw was president, was, and for a long period thereto had been, manufacturing a lard substitute, consisting of cotton seed oil which was hardened to lard consistency by the addition of a hard fat,—oleo stearine. This material was known under McCaw's brand of "Flake White." McCaw at that time, had never met Burchenal, but was slightly acquainted with Procter. D. R., page 302, Q313. It seems, according to McCaw's story that in February or March, 1908, Procter called at McCaw's New York office, showed him a sample of oil which had been hydrogenized by Kayser, and in effect asked him if he would substitute the hydrogenized oil for oleo-stearine in making up some lard substitute. McCaw, now largely interested in the Procter & Gamble Company, says that, at, the time he said he thought the material would be unsuitable; but naturally his recollection on this point would tend to be influenced by his interests. But Procter has not "the slightest remembrance" of what he said to McCaw, and could not "relate the circumstances" of the meeting with McCaw. D. R., page 213, Qs. 30-35. He gave no hint or instructions to McCaw as to what McCaw should do—how to mix the hydrogenized fat and cotton seed oil or the proportions—but left the whole matter to McCaw. Burchenal had no

hand in the matter whatever, and it does not even appear that he claims to have asked or suggested to Procter to see McCaw, or to have McCaw make any compound.

Subsequently, in May, 1908, as previously stated, 450 pounds of Kayser's hydrogenized oil was sent to McCaw who substituted it for oleo-stearine in the production of a lard substitute, and produced 3,000 pounds of such lard substitute, in three batches of 1,000 pounds each. The batches varied somewhat in the proportions of the hydrogenized fat to the liquid cotton seed oil, one batch containing 10% of the fat, another 12% and a third 14%.

Q277. You were left to your own resources in making up the mixture?  
A. Oh, absolutely, at that time. McCaw, D. R., page 295.

McCaw testified that he followed the usual method of mixing the fat with the cotton seed oil according to the titer of the former, first melting the fat, and, after blending it with the oil, subjecting the mixture to the usual deodorizing, refrigerating and aerating treatments to which Flake White had long been subjected. McCaw was evidently proud of his reputation as a lard substitute manufacturer, and of his Flake White, and did not care to put out a lard substitute which was, according to his notions, not as good as Flake White. He was, he says, not satisfied with these three batches made in May, 1908, because he regarded them as "unmerchable," the texture was "grainy, lumpy" and it was "entirely too dark." On being questioned, he refused to state how the batches were deodorized, as this process was and is "a secret one" which they still guard "jealously." He says the material then made was sold in bulk to some soap-makers—whose names he does not remember. McCaw said he cooked some biscuits with the compound and fried potatoes, but that they were unsatisfactory. Burchenal at one time said that the McCaw experiment was a "failure," and that the material appeared "stringy" but he was "not a judge of the material, *not having had any experience* (italics ours). Compare these statements of McCaw and Burchenal's, however, with this further statement of Burchenal in contradiction (italics ours).

Q1025. Referring now to the sample of the mixture that Mr. McCaw made, using the hydrogenized cotton-seed oil which was sent him in the early part of May, 1908, which sample you said you thought you saw,—was that sample edible? A. *I presume it was.*

Q1026. That is, you regarded it as an edible fat product?

Above question is objected to as incompetent and irrelevant.

A. *I do not recall any tests being made on it; I merely presume that it was.*

Q1027. So far as the edibility of it was concerned, however, you were satisfied that it was edible?

Above question is objected to as incompetent and irrelevant.

A. There was no question raised in my mind as to its being edible.

Q1028. I show you a certified copy of the Declaration of Interference dated January 3, 1913, in the matter of the Interference of Ellis vs. Boyce vs. Burchenal, No. 35,642 in which your application Serial No. 591,721, which subsequently eventuated into Letters Patent No. 1,135,935, was involved, and in which it appeared that the issues were as follows:

## Count 1:

An edible oil product comprising hydrogenated cotton-seed oil and edible oily material blending therewith.

## Count 2:

An edible oil product of lard-like consistency comprising edible hydrogenated oil and edible oily material blending therewith.

I also show you a certified copy of the preliminary Statement of John J. Burchenal, dated February 15, 1913, filed in that Interference, in which you state that the food product set forth in the Declaration of Interference "was made up in the latter part of May, 1908, and tested at Macon, Georgia." Was that material of which a sample was sent you by Mr. McCaw, the product to which you referred in that Preliminary Statement? A. I presume it was.

Q1029. Then at the time of swearing to that Preliminary Statement, you regarded the material which had been made by Mr. McCaw at Macon, Georgia, using the hydrogenated oil which was sent him in the early part of May, 1908, as an edible product of lard-like consistency, comprising edible hydrogenated oil and edible oily material blending therewith, did you? A. I think so.

Q1030. Well that is the fact, is it not? A. The fact was that I thought so.

Q1031. Do you still think so? A. I still think so.

*Note.* That the hydrogenized cottonseed oil referred to was produced by Kayser, with Kayser's process and by Kayser's machine, on Kayser's own initiative, and was edible, and that Burchenal makes no claim of having caused it to be sent to McCaw. It may well be that Mr. Kayser suggested that this be done.

Kayser continued to produce his hydrogenized product, and, in August, 1908, a second batch of 1,000 pounds thereof was sent to McCaw at Macon, and 10,000 pounds of compound was made, by mixing the hardened fat with cotton seed oil, about the first of September. McCaw made some changes in the speed of the refrigerating rolls, and the speed of the picker shaft in the aerating apparatus, and while the compound was improved in appearance over that made in May he still regarded it as "not merchantable." But the hydrogenized fat was substantially the same as that which had previously been sent him, and both were edible, for Burchenal testified (*italics ours*):

Q1060. Now, at the time you sent, or Mr. Procter or the Procter & Gamble Company sent that first batch of hardened cottonseed oil to Mr. McCaw, had you made up your mind *that hydrogenized oil produced by Kayser was an edible oil?*

A. I had.

\* \* \*

"Q992. \* \* \* A. \* \* \* As a matter of fact at the time, March 5, 1908, Mr. Kayser's real interest was centered in the production of a catalyst. *He had no question about being able to make a hard fat when his catalyzer was right.*

Q993. And he knew that he could make a fat of any consistency he wanted, if his catalyst was right?

A. I suppose so.

\* \* \*

During the fall and winter of 1908 and 1909, Procter & Gamble Co. erected a large plant for the hydrogenation of oils—reproducing on a large scale the small plant which Kayser made in December, 1907, and January, 1908. This plant was started in operation February 15, 1909.

Anderson and Kayser were at work on the large plant for about six months, and, as Anderson says, it was "the equivalent of the first plant on an enlarged scale," and in March, 1909, a carload lot of the Kayser hardened cottonseed oil was shipped to the McCaw plant in Macon. This hardened cottonseed oil shipped in March, 1909, Burchenal says was no different from that made by Kayser and shipped to McCaw in May, 1908:

\* \* \*

In the meantime Procter & Gamble Company had purchased in January, 1909, the McCaw Manufacturing Company, and had secured the services of McCaw. The carload of hardened fat was made into lard compound by McCaw, by mixing it with cottonseed oil and oleo stearine, substituting the hardened fat for a portion of the oleo stearine. This compound, McCaw did not consider as good as his regular Flake White, as he was "uncasy about the quality" but it was placed on the market and sold under the brand "Flake White."

\* \* \*

The oleo stearin was entirely left out of Flake White in 1912, but no one ever knew of the difference between the original Flake White, consisting of cottonseed oil and oleo stearin, that consisting of cottonseed oil, oleo stearin and hydrogenized fat, and that finally consisting of cottonseed oil and hydrogenized fat.

\* \* \*

In Burchenal's long examination, he was given over and over again an invitation to say what *he* did, what *he* contributed to Kayser's product, and the most that he could say was, and that is apparently his whole case—that he made up his mind that it was edible. Not as a result of food experiments, or cooking experiments, but only that he *thought* it might be edible. He does not say *he* sent the material to McCaw or suggested its being sent. It was Kayser's product, and it was Procter who saw McCaw and sent the product to him.

\* \* \*

We tried to get Kayser to tell *his* story, but he was in a German detention camp in England, and refused to talk (Barrows' testimony). But Kayser's friend, Clarence Von Phul, with whom Kayser boarded in Cincinnati from November, 1907 to March, 1908, testified that Kayser knew *his products were edible*, as follows (italics ours):

\* \* \*

Q13. Did you know where Mr. Kayser was employed at that time?

A. Procter & Gamble Company, at Cincinnati.

Q14. What work was he doing, if you know?

A. *He was getting up a patent for a food product, he so informed me.*

\* \* \*

Q17. Just what did he tell you about this matter?

A. *He said that he was producing a food product from cotton-seed oil by a chemical action.*

\* \* \*

Von Phul was sufficiently in Kayser's confidence that Kayser had him make the sketches or drawings which were used by the patent solicitor in preparing the drawings for Kayser's patent No. 1,004,035, which was applied for March 20, 1908.

Von Phul said that the sample Kayser showed him "looked like tallow" but Kayser said it was a food product.

\* \* \*

Kayser had no confidants except Von Phul, no one else knew about his process and his products except Burchenal, his right-hand man Anderson, and Procter, who seems to have a poor memory. The whole thing was kept a secret by the Procter & Gamble Company, who "would have arrested any one seen talking with Kayser," and the secrecy is maintained to this day. But enough has been drawn out of those men, after Judge Hollister issued an order to compel them to answer, to show that if any credit is due to any one at Procter & Gamble Company's factory, for the production of food products by the hydrogenation of cotton-seed oil, it is due to Kayser, who brought the process and products from Crosfields' in England. Procter & Gamble had to square the matter with Crosfields' later on, but, as Kipling says, "that is another story."

Kayser returned to England in July, 1910, and when he was out of the country Burchenal filed the application for the patent in suit.

\* \* \*

In any event this defendant has proved that Burchenal made no inventive act, and made no invention or discovery whatsoever. Burchenal does not intimate that *he* suggested any after treatment for the hydrogenized product, or the use of a refined oil, or even its use in the manufacture of a cooking fat, or that he made any tests in cooking or otherwise. He knew nothing about the subject except what Kayser told him.

\* \* \*

#### "LARD-LIKE" FATS

The plaintiff may contend that Kayser's semi-solid product is not "lard-like."

If "lard-like" has any special significance in the Burchenal patent it infers a product which is low in linolin and high in olein, and with not over 25% saturated fats.

Burchenal, in his testimony, however, thus variously defines "lard-like" (italics ours):

Q486. How did you know whether or not they (partially hydrogenized products) were lard-like, without testing?

A. *From appearance.*

\* \* \*

Q488. What is the physical appearance of lard?

A. Well, it is a material that is, according to my views of lard, in a general way, it is something that is soft to the feeling, at a normal temperature, has a translucent whitish appearance, it is not hard or brittle and it has a certain kind of plasticity to it. It is not granular, but lends itself to moulding. I suppose you might say it is homogeneous. It is of peculiar quality, I suppose; it is the one that of all the natural fats has made it adaptable for domestic purposes in cooking.

Q489. How does that description which you have given differ from the lard compound?

A. Lard compound is quite different in appearance. Lard compound is softer than lard itself; the fats have not the same characteristic; lard compound is not of translucent appearance; it has a foamier look to it; it has not the same consistency. I don't think anybody that is familiar with both of them would confuse one with the other.

\* \* \*

#### BURCHENAL MADE NO CONTRIBUTION TO THE ART

He was not versed in the manufacture of lard substitutes, for, as he says, "I was not altogether familiar with the manufacture of compound."

He knew nothing about the hydrogenation of oils except what he learned from Kayser. He never saw hydrogenized products until Kayser showed them to him. So far as the Record shows, he has never himself hydrogenized any oil or directed or supervised the hydrogenation by others.

He was not, so far as the Record shows, a scientist, a chemist, or even one "skilled in the art" of making food products. Up to March, 1909, the Procter & Gamble Company made soap, not food products.

Burchenal admits that

- (1) He does not know the "saponification value" of cottonseed oil.
- (2) He does not know whether hydrogenization changes the saponification value of cottonseed oil.
- (3) He does not know the temperatures to which the refrigerating rolls for the product must be chilled, but he thinks the temperature of the rolls is an important feature in making the product "lard-like."
- (4) He does not know what effect a variation in the pressure during hydrogenation may have upon the product.
- (5) He does not know what effect a variation in the temperature during hydrogenation may have upon the resultant product.
- (6) He does not know what effect a variation in the proportion of catalyst to oil, during the hydrogenation, may have upon the resultant product.
- (7) He does not know what effect a variation in agitation during hydrogenation of oil may have on the resultant product.
- (8) He does not know the proportions of hardened or hydrogenized fat to oil, as they were mixed by McCaw in 1908; he didn't see the mixing; he does not know what was done with the material made by McCaw; he does not know

whether the hydrogenated fat sent McCaw was deodorized or whether McCaw deodorized the compound made therefrom; and he does not know what tests McCaw made.

(9) He does not recall (and this after long fencing on his part) whether he knew the proportions of the component glycerides of the product described in the patent in suit, before he filed the application for the patent in suit.

Q828. Under date of November 20, 1912, the composition of the partially hydrogenized oil obtained by analysis of the product prepared in the manner described in the specification of the patent in suit was stated to be as set forth in lines 10 to 18, inclusive, page 2, of your Letters Patent in suit. Did you make the analysis?

A. I didn't.

Q829. Did you see the analysis made?

A. No.

Q830. Or check them?

A. No.

Q831. Do you know who made them?

A. No.

(10) He does not know who made the "re-determinations of the melting point and titer corresponding to the iodine value of 55 and 80 in partially hydrogenized cottonseed oil" given in the affidavit of Feb. 17th, 1915, which was his affidavit required by the Examiner before allowing the patent in suit but *supposes* "that things were based on our determinations at Ivorydale," but he did not make them and does not know who did.

(11) Burchenal further admits on examination that he does not know at what melting point the product of his patent in suit would cease to be "lard-like," or whether the product having an iodine value of 55 would be a semi-solid at ordinary temperatures.

(12) Again he does not know what is necessary to produce his alleged product. (*Italics ours.*)

Q856. In the production of a partially hydrogenized cottonseed oil what factors are necessary to insure in the product a high olein content and a low linolin content?

A. I can't tell you.

Q857. You mean that you don't know?

A. *I don't know.*

Q858. *And never did know?*

A. *Never did know.*

(13) Burchenal admits that he does not recall giving instructions to McCaw as to the products McCaw made in 1908. He does not recall making or supervising any cooking tests with hydrogenized oils, until after Flake White, containing hydrogenized oil was put on the market following February 15, 1909.

NOTE.—The hydrogenized fat was placed on the market before any cooking tests with them were made by Burchenal, who was ignorant of McCaw's tests. And there was no material difference between that hydrogenized fat and the fats which had been brought to this country by Kayser, and which were made here, in January, 1908, by Kayser.

(14) Burchenal likewise admits that he does not know whether animal oleostearin is edible—he presumes it is but is not certain.

(15) He says he does not think *any* animal or vegetable fatty acid or glycerides of any animal or vegetable fatty acids when hydrogenized, are suitable for use as food products, Q1005, D. R., p. 248, and denies that a food compound closely simulating lard can be made by a mixture of any oil and a hardening agent produced by hydrogenating *any* oil or liquid fat.

(16) He does not know whether the iodine value of a product is one of its physical constants.

(17) And he never effected the separation of the liquid fatty acids of any cottonseed oil treated by hydrogen.

(18) He was asked when *he* first produced a homogeneous lard-like food product consisting of an *incompletely* hydrogenized oil.

Why I had done a good deal of experimental work on the material; I think I am safe in saying that the date on which that material was first produced in any appreciable quantities was after April 26, 1910, and in all probability, prior to July 1, 1910.

\* \* \*

(But Kayser had already disclosed to Burchenal semi-solid products of hydrogenated cotton seed oil—those he brought from England, and those made by him March 5, 1908, which had melting points of 42° C. and 43° C.)

(20) Burchenal was asked *what* experiments *he* made with a mixture of the hard Kayser product and cotton seed oil, if any, and this is how he testified:

Q895. Now, when the first experiments were made with hardened cottonseed oil, by compounding it with other cottonseed oil, what did you do to the product, other than mixing the ingredients together? A. *I don't recall that we did anything beyond the mixing of the oil.*

\* \* \*

The fact is that really Burchenal had nothing to do with any experimentation involving hydrogenization that was going on, in spite of vague references to the "experiments" "we" made.

Morrison let the real truth slip out. He was asked:

Q169. *Who was actually doing the experimentation in hydrogenizing oils in the laboratory?*

A. *At what period?*

Q170. *Prior to Nov. 10, 1910?*

A. *Mr. Kayser up to the time he left in 1910, and after that Mr. Graff with the assistance of boys who were employed in the laboratory.*

Kayser left this country in July, 1910.

(21) Burchenal introduced the new matter regarding the proportions of component glycerides in his application for patent on November 20, 1912. He admitted that *he* had not ascertained these proportions by his own work but through the work of others, but he didn't know how they were ascertained, or who found them out, or when he got the information.

Morrison says *he* doesn't know who made the determinations, Qs86-88, D. R., pp. 326, 327, from which the percentages of component glycerides were figured,



but that he himself made the figures, that they were made from some memoranda which he has lost, and he would or could not say positively that the proportions or percentages were worked out prior to the filing of the application for the patent in suit.

*But it was Kayser* who was "doing the experimentation in hydrogenizing oils in the laboratory."

If anything is clear, it is that while Burchenal talks vaguely of "experiments," which "we" made, *he* really never did anything that can be placed to his credit, or which shows any inventive act or deed on *his* part. His general ignorance on the subject is manifest. His admissions demonstrate lack of originality. One will search the record in vain to find any evidence entitling him to be ranked as an inventor. It is only to *inventors* that valid letters patent can be granted under the statutes. Kayser, so far as Burchenal was concerned, was the source of all of his information. Kayser disclosed to him the process, the apparatus, the edible product, and Kayser carried on exclusively the experimentation in hydrogenation without any suggestion from Burchenal. Suppose there were a direct contest between Kayser and Burchenal as to the inventorship of the white or yellowish semi-solid produced by the partial hydrogenation of cottonseed oil—could there be any doubt as to the outcome? *The very first product which Kayser showed Burchenal was such a product and Burchenal admits it was edible.* Would any Court give priority of invention to Burchenal? If priority could not be awarded Burchenal in that case he certainly cannot be held to be the inventor of that same product in the case at bar.

The record clearly shows that Burchenal has no standing as an inventor and consequently the patent issued to him is void.

\* \* \*

In a discussion of the file wrapper and contents of the patent in suit, the following statements appear in defendant's brief:

What instantly strikes one familiar with the Kayser patents, and the processes therein described, and the solid and semi-solid hydrogenized cottonseed oils produced by Kayser, is that the Burchenal specification as filed described only what Kayser had disclosed to him. The sample of hydrogenized oil which Kayser brought from Crosfield & Sons had a melting point of 39.3° C. and an iodine value of 52.26, a little less than 55 which Burchenal mentioned as the lower limit in his original specification. One is also struck with the fact that the *preferred melting point* of the semi-solid product originally described by Burchenal, is the melting point of one of the two products produced by Kayser on March 5, 1908, the other Kayser product having a melting point of 43° C. which was the upper limit of the melting point range originally given by Burchenal.

On November 26, 1910, before the case was acted on by the examiner, the following claim was added to those on file.

### 3. A semi-solid hydrogenized oil.

On the 13th of December, 1910, the claims were rejected by Examiner Ely on U. S. patent to Schwoerer No. 902,177, the Herforder (Normann) German patent No. 141,029 and the Erdmann German patent No. 211,669. In explanation Examiner Ely said in part:

The composition of lard and of cotton seed oil as to the glycerine olein and stearin that they contain is well known. To make a product from

cottonseed oil that shall simulate lard, the content of stearin should be increased.

After citing the patents referred to, Examiner Ely further said:

It is thought therefore that if the problem of simulating lard from cottonseed oil were presented to an oil chemist, an incomplete hydrogenation of the cotton seed oil would at once suggest itself to him as a solution of the problem. All the claims are accordingly rejected on the above ground of lack of invention."

Burchenal waited until the last moment of the statutory period of one year allowed for the filing of an amendment to save the case from abandonment, and on December 13, 1911, filed an amendment cancelling claim 3.

By the cancellation of this claim he admitted that semi-solid hydrogenized products were old in the prior art. The prior patents to Normann and Erdmann had disclosed semi-solid products produced by the partial hydrogenation of both animal and vegetable oils.

The argument filed as a part of the amendment said in part:

Applicant does not allege that his product is identical with lard, for it may be and probably is impossible to artificially reproduce lard. . . . Applicant appears to be the first to determine and set forth the advantages and properties of a fractionally-hydrogenized product, and *his claims do not even cover such product broadly but are limited to a product having a definite degree of partial hydrogenation, giving it definite physical and chemical characteristics specified in the claims.* (Italics ours.)

(At this time Burchenal's claim 1 specified a range of 36°-43° C. in melting point, and claim 2 recited specifically a melting point of 40° to 21° C., in addition to the iodine value range of 55-80, etc. So Burchenal had conceded that a food product consisting of partially hydrogenized oil having melting points above or below the melting point range given by him and having iodine values below or above those recited by him, were not of his invention.)

On December 29, 1911, the Examiner a second time rejected the claims, citing the Kayser patents 1,004,035 and 1,008,474, and pointing out that Kayser described hydrogenizing cottonseed oil, and that Kayser's process could be arrested at any time during its progress to produce an incompletely hydrogenized article. He pointed out the fact that

*the physical constants given as to the product in claim 2 are not seen to define anything critical or decisive.* (Italics ours.)

and rejected the claims as defining nothing patentable over the disclosures in the Kayser patents.

(The Examiner was thus directing special attention to the following statements in the two Kayser patents.) (Italics ours.):

The time of treatment will vary with the progress realized and with the degree of saturation aimed at. Patent 1,004,035.

\* \* \*

Again Burchenal let the matter lie dormant for ten months and, on November 20, 1912, more than two years after he filed his application, filed an amendment in which he presented the new matter containing the specific reference to the

particular percentages of the component glycerids supposed to identify his product. Defendant's Exhibit Book, page 14. In the meantime Carleton Ellis had been granted a patent, No. 1,038,545, for a butter substitute by an Examiner in another division (No. 6) of the Patent Office separate from that in which Burchenal's application was pending. In this patent, Ellis pointed out the desirability of having his butter substitute melt at a temperature below the heat of the human body.

In the amendment, dated November 20, 1912, Exhibit Book, page 14, Burchenal presented present claims 5 to 7, inclusive, directed to the specific composition of his product, changed the numerals of his original claims 1 and 2 to 3 and 4, respectively, and presented two new claims copied from this Ellis patent. *Not for a lard substitute, but for a butter substitute, as follows:*

1. A *butter-like* composition comprising edible hydrogenized fatty oil.
2. A *butter-like* composition comprising edible hydrogenized vegetable oil.

In order to lay a basis for these claims in the new matter presented by amendment, there was included the phrase, "*but below the heat of the blood*" after the word "temperatures" in line 74, page 1, and line 26, page 2, of the printed copy of the patent.

By this same amendment he changed the preferred melting point of 41°-42° C. in his original claim 2 to 36°-43° C.

Burchenal's application was transferred to Division 6 to Examiner Lewers, who had permitted the Ellis patent to issue, and on December 6, 1912, Examiner Lewers wrote Burchenal that there was no basis in his application for the new claims 1 and 2 for a butter substitute. He pointed out that a butter substitute must have "a melting point considerably less than the temperature of the human body" so that it will melt in the mouth, whereas the *minimum* melting point stated originally by Burchenal was 36° C. (or 97° F.) was not "considerably below" body temperature, and the preferred melting point 41°-42° (105.8°-107.6° F.) "are much above the normal human body temperature." The Examiner accordingly rejected the new claims 1 and 2 both as "covering new matter" and because the product originally described by Burchenal was not butter-like.

Touching the new claims 5, 6 and 7 in which the proportions of component glycerids were recited, and the amendment to the specification setting them forth, the Examiner said:

The composition was not originally given and the Examiner has *no means* of determining that the compound having the properties set forth in the last paragraph of page, 1, and the first paragraph of page 2 (to wit, one having a melting point ranging from 36° C. to 43° C. preferably 41°-42° C.) . . . a saponification value of about 195, an iodine value ranging from about 55 to 80, and a titer of from about 35.5° C. to 42.5° C.) *would necessarily have the composition set forth in the amendment. The only ground upon which the statement of the composition can now be inserted is that the compound having the properties as set forth in the case as filed must have the composition alleged, and proof of this in the form of a proper affidavit must be filed. (Italics ours.)*

The Examiner again rejected original claims 1 and 2 on the Kayser patent, calling attention to line 15, page 1, and lines 95 to 102, page 2, of said patent. These lines have been quoted on pages 142-143 of this brief.

On January 10, 1913, Exhibit Book, page 21, Burchenal amended his new claims 1 and 2 by changing *butter-like* to "lard-like," and inserting the word *lard-like* in claims 3 and 4 (original claims 1 and 2). He accepted the Kayser patents as prior art. How could he help it, as we now know what Kayser had disclosed to him, and Burchenal has now admitted and conceded on the witness stand.

He said in the "Remarks" accompanying the amendment:

The product *originally* described, *having the melting point titer and iodine value* specified in original claim 2 *has the chemical composition set forth* in claims 5, 6, 7.

He urged that the product of claims 3 and 4 (original 1 and 2) was not anticipated because Kayser had not specifically described:

a *lard-like* food product, a semi-solid having a melting point ranging from 36° C. to 43° C.

Of course, the Examiner did not know that Kayser had produced products of melting points of 42°, 43° C. and did not know anything about Kayser's samples brought from Crosfields; so on February 15, 1913, he wrote a letter stating that when the supplemental oath was filed the case would be allowed.

March 17, 1913. Note Burchenal's next move. In claim 3, original claim 1, he cancelled the reference to the melting point range of 36°-43° C. and substituted a reference to the "iodin value ranging from 55 to 80." He said in his "remarks:"

these products have no sharp or definite melting point, and in view of the variety of melting point methods employed by chemists and the different values obtained thereby claim 3 has been amended to specify the range of iodine values of applicant's products rather than their melting-point range.

Thus he changed the specification in a way the examiner had refused to permit him to do—to insert a melting point temperature "*considerably lower*" than body temperature. He filed also an affidavit that the subject matter presented in his amendment filed November 20, 1912, had been invented before he filed his application, but this affidavit was in support also of the claims for a "*butter-like* product.

On May 27, 1913, the examiner suspended further action on the merits, since the companion application (which eventually resulted in patent 1,135,935) was involved in an interference with an issue (see claims 3 and 4 of said patent) over which the then claims 1 and 2 of the application of the patent in suit were "not patentable."

The case was then suspended until January 22, 1915, and on that date the examiner called attention to the fact that Burchenal had not yet filed the affidavit which the examiner had required on December 6, 1912, that the product as originally filed *must* have the chemical composition recited in claims 5, 6 and 7. He required the reference to the product as "congealing below the heat of the blood" to be stricken from the specification as amended.

There was, at this time, still in the specification, the original statement of the melting point range of 36°-43°, preferably 41°-42° C.; so Burchenal amended his case on March 5, 1915, by cutting out of the original specification the reference thereto.

\* \* \*

Burchenal also cancelled from the specification the reference to his product congealing below blood temperature.

Up to this time, there had remained in the original specification a paragraph to the effect that the product could be produced by mixing "unhydrogenized oil and a hard hydrogenized product having a melting point of 50° C." On this date, March 5, 1915, Burchenal cancelled this paragraph, cancelled his claims 1 to 4 (including the original claims and the first and second claims presented November 20, 1912), and presented the present claims 1 to 4 as they now appear in the patent.

Now, when the case was originally filed the only directions given to produce the "white or yellowish semi-solid" were to stop the reaction when the product on cooling had a melting point of 36° to 43° C.—preferably 41°-42° C., and these products were said to have an iodine range of 55 to 80. Burchenal *had not* said to "stop the reaction when the product has an iodine value of 55 to 80," but that a product having *those melting points* would have that range of iodine values, and he had persuaded the examiner to allow his claims because Kayser's patent had not specifically recited these melting points in referring to his "semi-solid."

Yet Burchenal in his amendment lowered the titer .5° C. and changed his specification in respect of the melting points, and reduced the whole range of 36°-43° C. to 33°-40° C.; that is, he had lowered it 3° C. (5.4° F.) so as to bring the range down to as low as 33° C. (or 91.4° F. instead of 97° F.), which is *very much below blood heat*, and thus he did the very thing which the examiner had said he would not be permitted to do.

He said in his "remarks" (italics ours):

Applicant's affidavit filed herewith, conforms to the requirements of the examiner. It also embodies a more accurate *redetermination of the melting point and titer* of products prepared from cottonseed oil and having the described range of iodine value. While *the new figures do not differ substantially from those originally given, it is thought desirable to substitute them.*

\* \* \*

The history of the prosecution of the Burchenal application as shown by the file wrapper and contents of the patent in suit is a strange one. The case had been transferred from the division of the Patent Office headed by Dr. Ely to Division 6 headed by Mr. Lewers. Most vital changes were made in the specification and claims—and finally without a supporting or supplemental oath, the patent containing these changes and the new claims in suit, was permitted to issue.

These claims were drawn after the defendant's product was on the markets

From a consideration of the file wrapper and contents, one thing is certain;—Burchenal insisted that his product had and must have 20-25% stearin, 65-75% olein and 5-10% linolin.

\* \* \*

Another thing is certain. Burchenal changed the description of his process which originally told one attempting to produce the product to stop the reaction when the semi-solid product on cooling, had a melting point of 36°-43° C., preferably 41°-42° C., so that as amended and issued the patent contains a wholly inconclusive and ambiguous statement to the effect that the operation is stopped when the oil has been converted into a product which cools to a white or yellowish "*semi-solid more closely resembling lard than do the commercial mixtures of cottonseed oil and animal oleo stearin . . .*" (lines 89-94, page 1 of the printed patent).

He thereby renders his patent vague and uncertain in its description how to make or compound the product and leaves one to experiment.

Still another thing is certain. Burchenal lowered the melting point range of his alleged new product 5.4° F. and the titer range .5° C. and thus departed from his original disclosure, without a supplemental oath.

Patents in which new matter is thus inserted without a supplemental oath, have uniformly been held to be invalid.

\* \* \*

We confidently assert that the proceedings in the Patent Office prior to the issuance of the patent in suit, were such

(1) That having insisted that his alleged new product has a definite chemical composition, and no other, he cannot be heard to deny it;

(2) That nothing can be held to infringe his claims which does not have that definite chemical composition; and

(3) That Burchenal made radical changes in his specification and claims as originally filed, which were unsupported by his original disclosure, and that as a result his patent is void.

#### COMPARISON OF THE PATENTED PRODUCT WITH COMMERCIAL LARD SUBSTITUTES

Considering the Burchenal patent from the point of view advanced by Dr. Baskerville that the purpose of the patentee is to increase the proportion of solid fat, in order to secure the semi-solid consistency, it is shown by the record that there is no material difference between the product therein set forth as so considered, and those lard substitutes which for many years have been commercially on the market. In fact this is conceded by plaintiff's experts, Dr. Baskerville and Mr. Morrison.

The first paragraph of the specification reads as follows:

This invention is a food product consisting of a vegetable oil, preferably cottonseed oil, *partially hydrogenized* and hardened to a homogeneous white or yellowish semi-solid closely simulating lard.

If the words italicized—"partially hydrogenized" be omitted, that description fits what are known as "lard compounds" or "lard substitutes," such as "Jewel compound," which has been made commercially by Swift & Company since 1890, and of which, according to Mr. Richardson's testimony, Swift & Company produces between two hundred and fifty million and five hundred million pounds annually. T. R., page 553, Q15. Such lard substitutes consist of cottonseed oil hardened to a white or yellowish semi-solid simulating lard, by

the addition of 10 to 15% of oleo stearin, which is a hard white substance produced by expressing the oil from beef tallow. This substance furnishes the additional stearin necessary to harden the cottonseed oil to the desired stiffness or semi-solidity.

Mr. McCaw testified that for many years prior to 1908, the McCaw Manufacturing Company manufactured a lard compound known as Flake White, which consisted of cottonseed oil hardened or stiffened to lard consistency by the addition of high-grade oleo stearin having a titer of 53° C., in the proportion of 20% of oleo stearin and 80% refined bleached cottonseed oil. D. R., p. 132, Q21, Q26. The proportions of cottonseed oil and oleo stearin were varied according to the season of the year, more of the stiffening agent being added in the summer than in the winter.

\* \* \*

The record further shows that the substitution of cottonseed oil, hydrogenized to a melting point of 55° to 60° C., for oleo stearin, in the manufacture of Flake White, made no material change in the resultant product, and customers never knew the difference.

\* \* \*

It is clear then from the foregoing that, as a lard substitute, and for all purposes to which such materials are employed, there is no practical difference between a compound containing oleo stearin and one containing hydrogenized oil of the same or similar degree of hardness or solidity.

Now, it is customary in the manufacture of lard substitutes, whether oleo stearin or hydrogenized fat be added to the oil to stiffen it, to vary the proportion of the stiffening agent according to its titer or melting point.

\* \* \*

It appeared from the testimony at the trial that it makes no difference, so far as practical results are concerned, whether the cottonseed oil is stiffened or hardened by solid fats produced by partial hydrogenation, or by the addition of oleo stearin, or by the addition of hydrogenized fat. Both Dr. Baskerville and Mr. Morrison agree on this.

\* \* \*

#### *Patent not Granted on Theory of Added or Increased Stearin.*

In the foregoing analysis of the patent in suit we have assumed the theory, advanced by Dr. Baskerville, that the only purpose set out in the patent as the result of partial hydrogenation is the addition of or increase in the proportion of the solid fats or saturated glycerides. That, however, is not the theory on which the patent was granted, and in fact is contrary to the plain and unmistakable terms of the specification itself. Dr. Baskerville tried to give the impression that the patent points out the addition of the glyceride of *stearic* acid rather than palmitic as the vital feature in the patented product. But there is not a single word in the specification stating that solid fats or stearin are *added* or are *increased*.

\* \* \*

The whole stress in the patent, as shown, is placed on reducing the linolin to 5 to 10% and increasing the olein to 65 to 75%. Not a word is said directly about "increasing" the solid or saturated fats.

Moved by the exigencies of the case, and confronted by the triangular charts produced by Dr. Walker and Mr. Richter which were predicated directly on the three components specified in the patent in suit, and which prove the chemical dissimilarity of Kream Krisp and the product of the patent in suit—Dr. Baskerville hastily built up a theory of “added stearin.” Unfortunately for him he based his whole conclusions upon a fundamentally wrong analysis of cottonseed oil given in lines 18 to 23, page 2, of the patent in which the percentage of saturated glycerides is given as 17%. So far as is known there never was such a cottonseed oil having the percentages of component glycerides given in the patent. Dr. Baskerville had never seen one, he admitted, nor had Morrison or any one else. Dr. Baskerville evidently had not read Morrison’s deposition taken at Cincinnati in which he explained that that analysis was a blunder.

\* \* \*

Morrison also testified that the cottonseed oil being used at the time he made that analysis had iodine values of 108 to 110, and that the iodine values of the liquid fatty acids ranged from 147 to 148. He gave an analysis of the oil like that being used, as 48% linolin, 29.6% olein and 21.8% saturated fats.

It is of record, as admitted by Dr. Baskerville, that ordinary cottonseed oils contain from 20% to 25% saturated glycerids.

\* \* \*

To support his theory of added fats, Dr. Baskerville produced some charts IV, V and VI, purporting to show how the solid fats were increased in the product of the Burchenal patent from 17% up to 20 to 25%—but his charts, as he was forced to confess on cross-examination, were based upon the fundamentally wrong analysis of the cottonseed oil given in the patent in suit, and utterly disregarded the statement of the patent that the decrease in linolin and increase in olein were what it was desired to accomplish. Dr. Baskerville tacitly admitted on direct examination, when he presented his charts that they were illogical.

\* \* \*

With Dr. Baskerville’s admissions and concessions, his charts are swept into the discard and with them his theory of “added stearin” being the predominating feature of the patent in suit.

It is self-evident that with the product of the Burchenal patent, being described in specific detail as having 20 to 25% of saturated fats, and with cottonseed oil having 20 to 25% saturated fats, there could be practically no change in the proportions of the saturated glycerids during the hydrogenation. For example, the oil which Morrison said they were using when he gave the analyses of the Burchenal product had 12.8% saturated fats. The samples of the average product as described in the patent had 23% saturated fats. In such case the saturated fats were increased from 21.8 to 23—a difference of 1.2%.

Nothing could be clearer, in the patent in suit, than that Burchenal did not want to increase the stearin, because he thought it was indigestible and of “small value as shortening.” What he said he wanted to do, and did, was to have a product with only 5 to 10% linolin and 65 to 75% olein.

\* \* \*

Unfortunately for Dr. Baskerville, he knew nothing of this previous testimony of Mr. Morrison, or he would not have been misled by his zeal on plaintiff’s behalf



to advance such untenable theories as to the patent in suit and to back them up by his erroneous charts.

\* \* \*

But in the case at bar the plaintiff is seeking to exclude the public from *one* use of the semi-solid hydrogenized oil under the claims sued on, though conceding that the public has the right to it for other uses. That is, by labeling it a "food-product" or calling it "lard-like" the plaintiff hopes to prevent the use in cooking, of the product which the public has the right to use in making soap, or candles or lubricants. It is just as though a manufacturer of hydrogenized semi-solid cottonseed oil products of a relatively soft consistency, such as that of lard, should fill two barrels with his product manufactured exactly as directed in the patent in suit and should label one of them "soap stock" and the third "lard substitute." He ships the soap stock to a soap dealer and he ships the other barrel labeled "lard substitute" to a food products jobber. According to the plaintiff's theory the original manufacturer would infringe the patent in suit when he made that part of the hydrogenized oil which he labeled as a lard substitute and sold to the food products jobber, and would not infringe the patent by marking the material "soap stock" which he shipped to the soap maker—a proposition which leads to the inadmissible conclusion that for one use or purpose the article of manufacture may be public property and for another use may be subject of a patent.

\* \* \*

So, while the plaintiff may have been the first in the United States to hydrogenize oil for making food products and soap stock in accordance with the process which Kayser brought to this country, and the first commercially to produce in the United States hydrogenized fats for culinary and soap making purposes, it really created no new industry, but merely brought into that old industry of making hardened oil lard substitutes, and the old soap making industry, a process which was then well known. The product of the patent in suit, while it might have been commercially new in the sense that it was produced by a process which had not actually been used in this country in producing like hardened cottonseed oil, until Kayser brought it here, was not patentably novel.

Moreover, it has not been established that the product of the patent in suit has ever been commercially manufactured and sold. That product, as has been repeatedly shown herein, must necessarily have not more than 10% linolin, not less than 65% olein and not more than 25% stearin. Crisco was not produced and placed on the market until May, 1911, some six months after the patent in suit was filed, and plaintiff's chemical superintendent has testified that it does not contain the proportions or percentages of the component glycerids recited in the patent as the supreme identifying test of the patented product.

Moreover, consider the enormous sums of money spent upon the advertising of Crisco: Taylor testified that in 1911, \$180,000 was spent for advertising, and \$400,000 each year thereafter in all,—the vast sum of at least \$2,000,000 during five years. That money was spent in full page or two page advertising in all the great national and weekly magazines; free cans of Crisco were sent to 15,000 merchants selected throughout the United States; every jobbing dealer in the United States was supplied or furnished with advertising circulars and also full-size samples of Crisco; an extensive campaign of street-car advertising was carried out in a dozen or more cities; bill poster and newspaper advertising

was carried on; and advertising by lectures delivered in various domestic science schools, and universities by authorities in domestic science.

Notwithstanding that tremendous and most expensive advertising campaign, the sales of Crisco at the end of the fifth year amounted to only one-eighth to one-fourth of the sales of another lard substitute made by Swift & Company,—“Jewel” compound or shortening.

The sales of Crisco therefore are not due to any peculiar excellence or superiority to the product, but to the campaign of advertising. In the present case, the plaintiff used an attractive trade-mark name “Crisco” which doubtless helped to make the advertising effective. Anything, that is not absolutely dangerous, can be sold in large quantities if more than \$2,000,000, is spent in advertising it.

\* \* \*

An argument based upon commercial exploitation fails, therefore:

First, because a new industry was not created, but on the contrary an old process was employed in an old industry to produce an old result;

Second, because the sales of Crisco were due, not to any intrinsic merit possessed by it, but to a stupendous advertising campaign, and the expenditure of enormous sums of money in advocating and inducing its purchase; and

Third, because the sale of Crisco is no criterion as to the novelty or utility of the product of the patent in suit, since Crisco does not meet the supreme identifying test prescribed in the patent.

\* \* \*

#### SHORTENING VALUES

(a) The specification of the patent says that solid fats such as the saturated glycerides of the fatty acids, stearic, palmitic, etc., “are of very small value for shortening,” lines 46-48, page 1. Defendant has shown by Dr. Bacon that the Ward Baking Company now uses only the hard fats having a high melting point as shortening in the manufacture of bread and that a remarkably small amount will suffice for the purpose. The McFarland patent No. 884,606, describes the use of a hard fat as a shortening agent as early as April 14, 1908, the date of its issue; and the use of stearine, mixed with acid phosphate, in baking powders and self-raising flour, is described in the Horsford patent of 1856 quoted by Judge Blatchford in *Runford Chemical Works vs. Lauer*.

Miss Hanko, the plaintiff's culinary expert, testified that, as to a hard fat, such as in Florolene, in which it is admixed with flour, she could see no objection to the hard fat as a shortening agent.

(b) The specification says that:

Oil, liquid at the ordinary temperatures, does not make the best shortening, because the oil remains liquid, keeping the food in a soggy condition, and the oil will even settle to the under part of the cooked product and soil the cloth, paper, or whatever it may come in contact with, page 1, lines 54-61.

This statement has been disproved by Dr. Walker, by Miss Hanko, and by Dr. Bacon, the latter further testifying that for many years large bread bakeries used only liquid oil in the manufacture of bread as the shortening agent.

(c) The specification states that:

It is evident, therefore, that oils or fats containing notable quantities of glycerides of linolic acid or of lesser saturation, are distinctly inferior as an edible product to those containing a minimum of these glycerides with a larger per cent of olein, page 1, lines 35-41.

Cottonseed oil contains a notably high percentage of linolin (48%) whereas olive oil contains a small percentage—less than 10% (see Walker's chart, No. 9)—and about 80% of olein, but common usage as a table oil shows that cottonseed oil is not "distinctly inferior" to olive oil. In Bulletin No. 505 of the United States Department of Agriculture dated February 13, 1917, of which, as a publication of the United States Government, this Court may take judicial notice, it is said, page 18:

With allowance for metabolic products, the coefficients of digestibility have been found to be for olive oil 97.8; for cottonseed oil 97.8; for peanut oil 98.3; for cocoanut oil 97.9; for sesame oil 98; and for cocoa butter 94.9 per cent. These values indicate that the vegetable oils studied, with the exception of cocoa butter, have for all practical purposes the same digestibility and are utilized as completely as the animal fats."

(d) The specification contains an analysis of cottonseed oil, which all of the experts agree is fundamentally erroneous, and which was, as has already been shown herein, based on a blunder by Mr. Morrison, who made the analysis. This needs no further elaboration.

(e) The specification states in effect that the product, having a range in iodine value of 55 to 80, contains "from about 1.5% to 2.5% of additional hydrogen more than in the non-hydrogenized material," page 2, lines 4 to 7, whereas Mr. Richter has shown that a partially hydrogenized cottonseed oil product with an iodine value of 80 contains 2.04% additional hydrogen and that a like product with an iodine value of 55 contains 3.75% additional hydrogen, more than in the original non-hydrogenized cottonseed oil. T. R., pages 603, Qs198-199. This was not controverted by plaintiff on rebuttal, and shows that the statement quoted from the specification as to the percentage of additional hydrogen is not founded on fact.

(f) The "puffing" or self-laudatory statements of the patent as to the lesser liability of the product, responding to the identifying tests of the patent, to become rancid than lard, and its capacity to be heated to a higher temperature than lard, and its being an "ideal" product for frying and better than lard as a shortening are incapable of proof, and even "Crisco" has not been shown by plaintiff to excel in the respects noted. Defendants on the contrary have shown, by Dr. Bacon, that Crisco turns rancid more rapidly than lard, Dr. Bacon, RDQ363, T. R., page 722, and by Mr. Richardson that the smoking point temperatures of lard and lard substitutes depend upon the deodorization of the products with live steam, and that this is true of all fats. The steam treatment drives off the volatile constituents of the fat, and raises the temperature at which the fat will begin to smoke when heated to high temperatures. Richardson, Qs37-43, T. R., page 558.

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## DEFENDANT'S PROCESS AND PRODUCT

Defendant's product, Kream Krisp, was first placed on the market in September, 1914, and by March 1st, 1915, the production was between one and two tons daily or at an annual rate of 300,000 to 600,000 pounds. Richter, pp. 207-208, T. R., 604, 605. Kream Krisp evidently came to the attention of the plaintiff soon after it was placed on the market, since in *February*, 1915, Burchenal wrote to the defendant that it was infringing its patents on "food products" though in point of fact he then had no food product patents. The application for patent in suit was pending, however—so he filed an amendment presenting present claims 1 and 2 on *March 5*, 1915, and lowered the melting point range, as originally given, doubtless with the hope of covering Kream Krisp.

Kream Krisp is produced by a wholly different process from that described in the patent in suit, the process of its manufacture being patented in Letters Patent to Hugh K. Moore, No. 1,121,860, dated December 22, 1914, applied for Feb. 26, 1914, and No. 1,184,489, dated May 23, 1916, applied for Oct. 31, 1914; Ex. Book, pages 62, 78. In the "batch process," as described in the Norman British patent, the Kayser patents and the patent in suit, a batch of oil with the finely divided catalyst mixed therewith, is heated, and by bubbling the hydrogen through the mixture, or agitating the mixture in the presence of hydrogen, there is caused a triple contact of a small body of catalyst, a large body of oil, and hydrogen—in consequence of which a certain "selective action" takes place and the linolin is first acted on by the hydrogen and converted to olein during the early stages of the process.

In the defendant's process the body of nickel catalyst—not chemically deposited on kieselguhr—but mechanically mixed with shredded asbestos, for the same purpose that hair is mixed with plaster to keep the layer from cracking,—is spread in layers between sheets of asbestos. These layers form a horizontal diaphragm in the hydrogenating vessel. Then oil heated to the desired temperature is sprayed by heated hydrogen from a rotating nozzle arranged above the diaphragm. Additional heated hydrogen is admitted to the vessel, or "capsule" as it is called, in the compartment above the diaphragm, so that the pressure above the diaphragm is greatly in excess of that below it. The fine spray of oil is therefore instantly driven through the porous catalytic diaphragm, and emerges therefrom, a portion of it being hydrogenized in its transit. The rotating nozzle sprays the oil on successive portions of the diaphragm,—the hydrogen alone sweeping through the other portions of the diaphragm and "revivifying" the catalyst by the absorption of the hydrogen on the nickel particles, or by uniting therewith to form an unstable hydride. The oil in passing through the diaphragm in the twinkling of an eye is acted on by the hydrogen in or on the catalyst—and since the catalyst is greatly in excess of the oil which is passing therethrough—the selective action of the batch process does not take place. On the contrary, a portion of the linolin is converted directly to a saturated glyceride (stearin) or else coincidentally a portion of the linolin is converted to olein and approximately a like portion of olein is converted to stearin. The result is that in the product of defendant the percentage of olein is substantially the same as in the original oil, while the stearin has been increased at the expense of the linolin. The resultant product contains the same kind of glycerides as the original oil (disregarding Dr. Baskerville's theory of mixed and simple glycerides) but they are in different proportions. Walker, Qs34-65, T. R., pages 492-

516. The cottonseed oil which is employed by defendant, is thus converted into a product like the sample can introduced in evidence by the plaintiff, as follows:

	Cottonseed Oil.	Kream Krisp.
Per cent saturated glycerides.....	31.5	28
Per cent olein.....	32.5	34.3
Per cent linolin.....	46	37.7

The range of the proportions of component glycerides given by Mr. Richter, who has charge of the analyses of Kream Krisp at defendant's factory, is as follows:

Per cent saturated fats.....	28-43
Per cent olein.....	34.3-37
Per cent linolin.....	33.3-37.7

The iodine values of Kream Krisp range from 83.8 to 94.7; the melting points range from 33.9° to 46.6° C.; and the titers range from 33.4 to 36.5.

In the particular product, on which the charge of infringement is based, to wit, that contained in the Kream Krisp can be offered in evidence by plaintiff as a part of Exhibit No. 2, the melting point is 35.7, the titer 23.85, the saponification value 194.5 and the Halphen test is negative. So far as the Halphen test is concerned, Richter testified that the sample was most unusual, since he had never before seen any of defendant's product which did not give a positive result on being tested, and explained that the oil was probably overheated.

On comparing the Kream Krisp with the original oil from which it was produced, it is very striking that the proportion or percentage of olein in the two is substantially the same, having been increased from 32.5% in the oil to 34.3% in the product—an increase of 1.8%. The linolin has been decreased from 46% to 37.7% or—8.3 and the stearin increased from 21.5 to 28% or 6.5.

	Cottonseed Oil.	Kream Krisp.
Saturated glycerides	$21.5 + 6.5 = 28$	
Olein	$32.5 + 1.8 = 34.3$	
Linolin	$46 - 8.3 = 37.7$	

The stearin or saturated glycerides have been mainly increased at the expense of the linolin. It cannot be said of the product that it is "high in olein"—within the purview of the patent in suit, because there was substantially no increase in the proportion of olein in the original oil; nor can it be said that the product is "low in linolin" since more than one-third of it consists of linolin. Only 8.3% of the original oil has been changed at all—1.8 has been changed from linolin to olein and 6.5 has been changed to stearin.

The remainder of the product has been unchanged. Whether the linolin was converted directly to stearin with only a small portion being converted to olein, or whether with the conversion of 8.2 parts of linolin to olein, 6.5 parts of olein is changed to stearin simultaneously therewith, is not known, and there is at present no known method of analysis by which this can be definitely ascertained.

## KREAM KRISP DOES NOT INFRINGE THE PATENT IN SUIT

So far as the proportions of the glycerides is concerned there is a profound difference between the two products—that of the Burchenal patent and Kream Krisp—as might be expected from the totally different processes by which they are produced. In addition, the iodine values are different, the titers are different, and the percentage of added hydrogen are different, all as will be seen from the following comparison, using Richter's figures:

	Burchenal Product.	Kream Krisp.
Iodine value.....	55-80	94.7
Melting point.....	33°-40° C.	35.7
Titer.....	35°-42° C.	33.85
Per cent saturated fats.....	20-25	28
Per cent olein.....	65-75	34.3
Per cent linolin.....	5-10	37.7
Per cent added hydrogen.....	1.5-2.5	.875
Saponification value.....	195	194.5

It will be noted from the foregoing that the iodine value of Kream Krisp is 94.7 as against the maximum of 80 given in the patent in suit; that Kream Krisp contains more than three times the maximum quantity of linolin stated in said patent, contains a little more than half of the minimum quantity of olein, and 3% more than the maximum quantity of saturated fats or stearin; that the titer is less than the minimum given; and that the per cent of added hydrogen is less than that given in the patent.

\* \* \*

*Kream Krisp does not meet a single identifying test pointed out in the patent in suit*, with the exception of its melting point, which is given by Richter as 35.7° C.; and as to the melting point be it remembered that when Burchenal first filed his application the melting point range was then given as from 36 to 43° and years afterwards changed to 33°-40° because Burchenal changed his opinion as to what the desirable melting point should be.

That Kream Krisp does not infringe the patent in suit is thus made clear.

It is true that Kream Krisp is used as a substitute for lard or butter, and is of such consistency that it may be used in their stead. In that respect it does not differ from the lard substitutes like Jewel and Flake White,—in fact, it is much more like Jewel compound than it is like the product of the patent in suit.

We call attention to a very significant statement in the patent to be found in lines 89-94, page 1, thereof, as follows:

In practice, the operation is stopped when the oil has been converted into a product which cools to a white or yellowish semi-solid *more closely resembling lard than do the commercial mixtures of cottonseed oil and animal oleo stearin*. . . . (Italics ours.)

Just what the italicized clause means, the patent does not state. It cannot mean that it is different from those compounds by reason of the *melting point*, or the *uses* to which they are respectively put, for therein lie no distinctions. It may mean that the Burchenal product is chemically more like lard, inasmuch as lard has 8% to 10% of linolin and is relatively high in olein. If the latter

is meant, then surely it excludes Kream Krisp, as will be apparent by a comparison of Kream Krisp with Jewel compound, which was one of the commercial mixtures referred to, and the Burchenal product.

	Kream Krisp.	Jewel.	Burchenal Product.
Per cent saturated glycerids.....	28	29.5	20-25
Per cent olein.....	34.3	29	65-75
Per cent linolin.....	37.7	41.5	5-10

The comparison can best be made visually by the triangular chart 402 (opposite page 575, of the Trial Record), produced by Richter, on which the products are graphically portrayed in the terms of these three components, to wit: saturated glycerids, olein and linolin referred to in the patent in suit. We here reproduce that chart which Dr. Baskerville admits is an "excellent" chart for indicating the percentages of the component glycerids. The cottonseed oil, Kream Krisp, Jewel and Burchenal's product are all located. A mere glance shows that Jewel and Kream Krisp are quite similar in their composition, and that both are equally remote from the composition of the Burchenal product. They also have approximately the same percentages of solid or saturated fats, although slightly more than Crisco.

Kream Krisp therefore is *directly excluded* from the scope of the patent, in addition to its failure to meet the identifying tests which are described in the specification thereof.

While, in the production of Kream Krisp, a portion of the oil is hydrogenized—it is by a process wholly different from that described by Burchenal. In fact, the record clearly shows that by the batch process and under the conditions of hydrogenation recited in the patent in suit Kream Krisp cannot be produced; and that by the process practiced by defendant it is impossible to produce the product described and defined in the patent.

\* \* \*

The patent in suit was pending in the Patent Office five years, during which the art progressed, and defendant's product had appeared on the market. After the application for patent was filed on November 10, 1910, and was rejected by the Examiner on December 13, 1910, Burchenal deliberately let the matter lay for one year until December 13, 1911, before replying to the examiner. The case was promptly rejected again on December 29, 1911, and again nearly eleven months passed by before Burchenal responded on November 20, 1912. In the meantime Ellis had secured patent No. 1,038,545 for a butter substitute, and then Burchenal tried to claim that his material was a butter substitute also. Burchenal, however, had described his material as melting from 36° to 43° C., that is, at a temperature *higher* than 36.6° C. (blood heat), whereas a vital characteristic of butter is that it melts *below* blood heat or body temperature. It was at this time that Burchenal presented the matter occurring in lines 13 to 74, page 1, of his printed specification, except that in line 64 he then referred to his product as "butter-like" instead of "lard-like." Burchenal was trying to grab Ellis' invention.

The Examiner however prevented that, refusing to permit Burchenal to call his product "butter-like" and pointing out that the preferred melting point as originally described by Burchenal, was 41°-42° C., and that it was very much *higher* than the melting point of butter. Foiled in his attempt to cover the

Ellis product, Burchenal then concluded that his own material was "lard-like" and inserted that expression for the first time in his claims. Later on, March 17, 1913, Burchenal took out of his claims reference to the melting point of 36° to 43° C. and substituted a reference to the iodine value instead. This was evidently done, because he wanted to get rid of that high melting point range of "36° to 43° C." in his specification, and it was his first move in that direction. He accomplished his ultimate purpose on March 5, 1915, when he substituted in his present specification a statement giving the melting point range from 33° to 40°, thus changing what he had originally sworn was one of the identifying tests of his product. As Morrison testified, Burchenal probably "changed his opinion afterwards" as to the preferred melting point of his product.

\* \* \*

#### CONCLUSION

Without attempting to summarize all the matters discussed in the brief,—for the length of which we apologize—we submit that we have, by the Record in this case, established beyond a shadow of doubt the several defenses set up in the answer as amended.

I. We have proved that prior to any date of invention that can be claimed for Burchenal, the hydrogenation of the various animal and vegetable oils to various degrees of saturation, or to various consistencies, had been explained fully, clearly and exactly by Normann, Bedford, Paal and Roth, Fokin and Kayser; that the phenomena of the reaction had been so minutely described that any oil chemist or technologist was able to reproduce the processes and reproduce the products, as was actually done by witnesses called by the defendant; that the earlier patentees and investigators had called attention to the freedom from rancidity which the hydrogenized products possessed, to their failure to respond to the Ikalphen reaction, to the various iodine values and consistencies which could be secured in the products, and to the fact that in the process no side reaction products were produced save nickel-soap, which was easily removable by known methods; and in fact that their various products were edible food products.

We have proved by the admissions and concessions of Burchenal, patentee of the patent in suit, that he was not the originator of the process of hydrogenation described in said patent; and that he makes no claim to the process, or any part thereof, described in the two Kayser patents, which process, as accurately and exactly described in one of the Kayser patents, is for hydrogenating cottonseed oil to a semi-solid of any desired consistency as determined by its iodine value or titer; that such process was disclosed to him (Burchenal) by Kayser; and that, in fact Kayser's products were edible including those brought to this country by Kayser.

We have further shown that Kayser disclosed to Von Phul, a disinterested witness, that he was working on a food product, and that he showed the first material produced by him in this country to Von Phul and told the latter it was his new food product, and this before Burchenal by "celebration" decided that Kayser's products were edible; we have shown that Kayser himself is not and was not available as a witness, and therefore could not be called to substantiate Von Phul's evidence; and we have shown that we have called, as hostile wit-



nesses, the only persons who did know of Kayser's work, namely, Burchenal, Anderson and Procter, whose testimony would naturally be biased on behalf of the plaintiff.

We have proved that Burchenal was not an independent inventor—that he was not one skilled either in the art of hydrogenation or in the art of fatty food products, that he could point to no single inventive act or deed that could be credited to him, and that his knowledge touching the production of semi-solid hydrogenized cottonseed oil was all obtained from Kayser—the fountain head of his information.

We have proved, by the very records of the plaintiff, the production by Kayser on March 5, 1908, of a semi-solid incompletely hydrogenized cottonseed oil having the melting points 42° and 43° C., one of which Burchenal described in his application as filed as the preferred melting point of his patented product which Kayser products were reproduced for the trial and were shown by Mr. Richter to be edible.

These facts established the invalidity of the patent for want of originality, novelty, and lack of patentable invention.

II. We have shown that the description contained in the specification and the claims in suit are lacking in that completeness, clarity, and exactness which U. S. R. S., 4888 requires as a condition precedent to the grant of letters patent, for we have proved both by the concessions and admissions of Burchenal and Anderson that it would be "a lucky strike" if one should produce the alleged new product by following the description contained in the specification, and by the testimony of Richter that he failed after repeated trials and experiments—following the description of the patent—to realize the alleged new product having the proportions of component glycerides stated therein.

We have proved by Burchenal's concession that even he does not know what factors are necessary to produce a partially hydrogenated semi-solid cottonseed oil which is high in olein and low in linolin with only sufficient stearin to make the product congeal, as defined in the specification, which the patent states is chief characteristic of the alleged new product.

These facts as proven establish that the patent is void.

III. We have established out of the mouths of the plaintiff's officers, including the patentee himself, that if there be any invention in the patent in suit (which we have shown is not so) it is the invention of Kayser, and that taking advantage of Kayser's absence from this country Burchenal patented the same. The facts as proven show that this was done unjustly and surreptitiously.

Wherefore, the patent in suit is void.

IV. We have proved by the proceedings in the Patent Office in connection with the filing and prosecution of the patent in suit, and by the admissions of the patentee, and the limitations imposed by the Commissioner acting through the Examiner that the alleged new product is necessarily limited to, and must contain, a specific percentage of component glycerides, to wit: 20-25% saturated glycerides, 65-75% olein, and 5-10% linolin, in addition to falling within an iodine value range of 55 to 80, and that no product can infringe the claims of the patent which does not meet both these identifying tests.

V. We have proved that new matter vitally changing the original description, and which was not predicated upon the original disclosure, and which was a radical departure therefrom, was inserted in the specification without a supplemental oath, and that the claims in suit were inserted without a supplemental

oath after defendant's product was in public use and on sale, by virtue of all of which the patent and said claims are invalid.

VI. We have proved that the manufacture of homogeneous lardlike food products consisting of cottonseed oil hardened to the consistency of lard, is an old and well-known industry; that giving to the oil its semi-solidity (1) by partial hydrogenation, (2) by the addition of hard hydrogenized fats, or (3) by the addition of the usual oleo stearine, enables it in either case to be used for all purposes as a substitute for lard in the culinary arts and for food purposes, and that in the last analysis (as distinguished from a product having the proportions of component glycerides recited in the patent), the amount of added solid fat is substantially the same, as conceded by Mr. Morrison, plaintiff's chemical superintendent. Hence, when the plaintiff makes the claim that it has started a new industry, it can only mean that it has extended into an old industry an old product produced by an old process. In this connection we have shown that "Crisco," which the plaintiff relies on as the product of the patent in suit, is not in reality that product, as it fails to meet the supreme identifying test of the patent, i.e., the proportions of percentage of component glycerids. And we have further shown that no one but the plaintiff really knows just how Crisco is made, and just what processes are used in its production. "Jealously guarded" secrets constitute a wall around Crisco, through whose unpenetrable thickness neither the Court nor this defendant nor the public can see to learn the real process of its manufacture. And we have further shown that millions of money have been lavished with a free hand to force Crisco on the public, in every way known to advertising managers, including the subsidizing of cooking school and university lectures. Yet, notwithstanding the spending of fortunes rivaling the lavish outlays of the Count of Monte Cristo, the annual sales of Crisco are less one-fourth than those of "Jewel" shortening manufactured by one concern—Swift & Co.

VII. By the record we have proved:

(a) That defendant's product does not meet the identifying tests set forth in the patent in suit, since it has neither the titer, the iodine value, the saponification value, nor the proportions or percentages of component glycerids, therein set forth as identifying the alleged new product.

(b) That defendant's product is not "lard-like" in the sense in which those words are used in the patent and that it neither smells nor tastes like lard, both the taste and smell thereof being different from the characteristic taste and smell of lard.

(c) That defendant's product is not made by the process described in the patent in suit.

(d) That the process as described in the patent in suit will not produce defendant's product.

(e) That defendant's process is a process covered by the Moore patents and is clearly unlike the process of the patent in suit, and that the reactions in the two processes proceed differently and produce markedly different results, and

(f) That defendant's process cannot produce the product of the patent in suit. Therefore, the defendant's product does not infringe the patent in suit.

VIII. We have shown in addition to the foregoing, that the equities in the case at bar are with the defendant; that its product is directly excluded from the scope of the patent in suit by the specification—since its chemical composition is substantially that of “commercial mixtures of cottonseed oil and animal oleo-stearin” from which the patented product is distinguished in the specification; that it embarked upon the manufacture of its product in good faith; that the claims in suit, unsupported by a supplemental oath, were deliberately inserted in the application after defendant’s product had for months been produced in large quantities and had gone into public use and had been inspected by the patentee.

We urge that the Court, in the protection of the rights of the public and of this defendant, should declare this patent in suit to be invalid or void, and thus preserve to the public and the defendant the inherent right to put to their natural uses those hydrogenized oils which it is conceded the patentee did not invent or discover.

And we urge that the Court should also find as a matter of both fact and law that defendant’s product “Kream Krisp” is not an infringement of the patent in suit.

We submit that on the grounds stated the bill should be dismissed with costs in favor of the defendant.

Respectfully submitted,  
MARCUS B. MAY,  
JOHN C. PENNIE,  
Counsel for Defendant.

New York, N. Y., April 23, 1917.

#### THE DECISION OF JUDGE AUGUSTUS N. HAND.

This suit is for infringement of patent No. 1,135,351, granted to the complainant as assignee of John J. Burchenal, on April 13th, 1915. The application for the patent was filed November 10th, 1910. The specification states that the invention is for a food product consisting of a vegetable oil, preferably cottonseed oil, partially hydrogenized and hardened to a homogeneous white or yellowish semi-solid closely simulating lard.

Claims 1 and 2 alone are in issue and read as follows:

1. A homogeneous lard-like food product consisting of an incompletely hydrogenized vegetable oil.
2. A homogeneous lard-like food product consisting of incompletely hydrogenized cotton-seed oil.

The special object of the invention is, according to the specification:

... to provide a new food product for a shortening in cooking in which the liability to become rancid is minimized and in which the components of such vegetable oils which are inferior and detrimental to use as such a food product have been to a large extent converted into a higher and more wholesome form. All such vegetable oils contain glycerids of unsaturated fatty acids and among these notable quantities

of fatty glycerids of lower saturation than olein. It is the presence of these glycerids of lower saturation that seriously affects the rancidity of the material. Oxidation is largely the cause of rancidity which oxidation weakens the fat at the point of absorption at the double bonds, and these glycerids of lesser saturation readily absorb oxygen from the air at ordinary temperatures while the more highly saturated glycerids, as olein, only absorb oxygen at elevated temperatures. It is evident, therefore, that oils or fats containing notable quantities of glycerids of linolic acid or of lesser saturation are distinctly inferior as an edible product to those containing a minimum of these glycerids with a larger per cent. of olein. On the other hand while it is important to get rid of the readily oxidizable glycerids of lower saturation, it is also important not to supply too large a per cent. of fully saturated glycerids.

... In manufacturing this product cottonseed or other vegetable oil is caused to chemically absorb a limited amount of hydrogen by reacting on the oil with hydrogen in the presence of a catalytic agent and at an elevated temperature. The oil is preferably agitated in a closed vessel in the presence of an atmosphere of compressed hydrogen, a catalyzer of finely-divided nickel carried by kieselguhr being maintained in suspension in the oil and its temperature being raised to about 155° C.

According to the present invention, the amount of hydrogen absorbed is carefully regulated and limited. In practice, the operation is stopped when the oil has been converted into a product which cools to a white or yellowish semi-solid more closely resembling lard than do the commercial mixtures of cottonseed oil and animal oleo-stearin while in many respects the product is superior to the best leaf lard as a shortening. It is not so liable to become rancid and the product can be heated to a considerably higher temperature than lard without smoking or burning. The high temperature to which my product can be raised without smoking or burning makes the product ideal for frying, inasmuch as a crust forms almost instantly on the food fried, which prevents any absorption of the shortening. A lard-like product thus prepared from cottonseed oil has a saponification value of about 195 and an iodine value ranging from about 55 to about 80. The product having an iodine value of 55 has a titer of about 42° and a melting point of about 40° C., that having an iodine value of 80 has a titer of about 35° and a melting point of about 33° C. While but partially hydrogenized, containing from about 1.5% to 2.5% of additional hydrogen more than in the non-hydrogenized material, it shows no free cottonseed oil when subjected to the Halphen test, thereby differing from all commercial lard substitutes containing this oil. It contains from twenty to twenty-five per cent of fully saturated glycerids, from five to ten per cent linolin, and from sixty-five to seventy-five per cent olein; and an average of a number of samples gives twenty-three per cent of saturated fats, seven and five-tenths per cent linolin and sixty-nine and five-tenths per cent olein, while the cottonseed oil before treatment contained seventeen per cent saturated fats, thirty-seven per cent linolin and forty-six per cent olein. It will thus be seen that I have produced an ideal food product which is high in olein, low in linolin and lesser saturated fats and with only enough stearin to make the product congeal at ordinary temperatures.

The complainant urges that Burchenal first taught the art that a partially hydrogenated vegetable oil, preferably cottonseed oil, was edible and was a useful lard substitute. It contends that prior to Burchenal's conception it was not known that hydrogenated cottonseed oil was edible and that the only processes then in use aimed at complete saturation and produced a hard non-edible product. Before discussing the prior art, I would say in general that Normann, whose patent will later be referred to, had already disclosed a method of hydrogenating oils, and had set forth in his specification that the process was progressive and involved "no secondary reaction." The method of adding cottonseed oil to beef stearin for use as a lard compound was well known and much used, as it still is. The hydrogenation of cottonseed oil resulted in a reduction of the fluid and substitution of the solid fats. Normann's patent, as well as various experiments of scientists, indicated that the addition of hydrogen to cottonseed oil would result in the reduction or elimination of the fluid and substitution of solid or partially solid fats. No one has shown that the product resulting from such hydrogenation was ever non-edible or unsanitary in any respect.

The British patent No. 10,783 (1887), to Joseph Sears was for a lard substitute composed of refined unbleached cottonseed oil and a fat adapted to give a stiffness to the compound corresponding substantially to that of refined lard. The specification provided that the temperature should be raised sufficiently to melt the fat or stearin, the heated ingredients mixed and then chilled rapidly so as to prevent crystallization and separation. This general process was well known in the art before the date claimed for the invention of Burchenal and indeed is referred to in the patent in suit. A very large market for such lard-like compounds exists at the present time and has existed many years past.

The British patent No. 1515 of 1903, to Normann discloses a process for the reduction of glycerides resembling that of the patent to Burchenal. Normann's patent says that:

The property of finely-divided platinum to exercise a catalytic action with hydrogen . . . is already known. . . . Recently Sabatier and Senderens of Paris have discovered that other finely-divided metals will also exercise a catalytic effect on hydrogen, viz.: iron, cobalt, copper and especially nickel.

By causing acetylene, ethylene or benzene vapour in mixture with hydrogen gas to pass over one of the said metals (which had just been reduced in a current of hydrogen) the said investigators obtained from the unsaturated hydrocarbons, saturated hydrocarbons, partly with simultaneous condensation.

I have found that by this catalytic method it is easy to convert unsaturated fatty acids into saturated acids.

This may be effected by causing fatty acid vapours together with hydrogen to pass over the catalytic metal, which is preferably distributed over a suitable support such as pumice stone. It is sufficient, however, to expose the fat or the fatty acid in a liquid condition to the action of hydrogen and the catalytic substance.

For instance, if fine nickel powder obtained by reduction in a hydrogen current, is added to chemically pure oleic acid, the latter heated over an oil bath and a strong current of hydrogen is caused to pass through it

for a considerable time, the oleic acid may be completely converted into stearic acid.

The quantity of the nickel thus added and the temperature are immaterial and will only affect the duration of the process. Apart from the formation of small quantities of nickel soap, which may be easily decomposed by dilute mineral acids, the reaction passes off without any secondary reaction. The same nickel may be used repeatedly. Instead of pure oleic acid, commercial fatty acids may be treated in the same manner. The fatty acid of tallow which melts between 44 and 48° C. has an iodine number 35.1 and a yellow colour will after hydrogenation melt between 56.5 and 59°, while its iodine number is 98 and its colour slightly lighter than before, and it will be very hard.

The same method is applicable not only to free fatty acids, but also to the glycerines occurring in nature, that is to say, the fats and oils. Olive oil will yield a hard tallow-like mass; linseed oil and fish oil will give similar results.

By the new method all kinds of unsaturated fatty acids and their glycerides may be easily hydrogenized.

The Normann patent clearly discloses that oils may be completely hydrogenized, that the process is progressive and that it involves "*no secondary reaction*," in other words, that cotton seed oil which starts edible remains so. The experiments and articles of Paal and Roth, which were alluded to at the trial, show that hydrogenization of oils including cotton seed oil was understood in the prior art.

Such being the state of the art, Edwin Cuno Kayser wrote Procter & Gamble from England that he had a process of considerable value and would like to talk to them about it; thereafter he came to America about November, 1907, bringing samples of hydrogenized cottonseed oil. He showed these to Burchenal, the superintendent of Procter & Gamble. As a result of his visit, he made an arrangement under a preliminary contract of January, 1908, to experiment upon the hydrogenized cottonseed oil as a substitute for lard. The first project was apparently to use hydrogenated cottonseed oil as a compound to be added to a percentage of beef stearin and cottonseed oil. Burchenal says he had done no work in connection with hydrogenizing cottonseed oil before he saw Kayser. He testified that:

Mr. Kayser went out to our factory and made sketches as to the apparatus that would be necessary to carry on this work and the apparatus was ordered at once; a little plant was installed for experimental purposes and I think it was ready to operate sometime in January or February, 1908. Deposition of Burchenal, page 11.

The defendant succeeded in obtaining contemporaneous memoranda as to some of Kayser's experiments from the records of Procter & Gamble. The first experiment was as follows:

Fat Hardening Process by E. C. Kayser.

First experimental lot was completed Jan. 17th, 1908. Fat treated—Summer Yellow Cotton-seed Oil. Used nickel Sulphate and Kieselguhr as described. Experiment was conducted by Mr. Kayser alone. He claims to have used about 1% Nickel Metal and 2% Kieselguhr.

M.P. of fat after 3 hrs.  $55\frac{1}{2}^{\circ}$  C.

M.P. of fat after  $6\frac{1}{2}$  hrs.  $60.3^{\circ}$  C.

Dr. Bender reports as follows:

Melting point of fat  $60.3^{\circ}$  C.

Hydrocarbons .33%.

Iodine value of fat 7.14%.

The fat does not contain free fatty acids. This material is much superior to the samples from J. Crossfield & Sons which showed an iodine value of 52.26 and a melting point of  $39.3^{\circ}$  C. (The laboratory sample melted at  $49.9^{\circ}$  C.) Their samples contained 5.12% free fatty acids and 2% hydrocarbons.

Mr. Kayser reports as follows: "The melting point of fatty acid, prepared from first lot hardened cottonseed oil is  $62^{\circ}$  C. This is several points higher than I ever got before. Presumably the composition of your oil differs somewhat from that of the oil I handled formerly."

Another experiment by Kayser of the date of March 5, 1908, was also obtained from the Procter & Gamble records in which the following melting points appeared:

5 hrs. at ordinary pressure  $42^{\circ}$  C.

$1\frac{1}{2}$  hrs. at 60 lb. pressure  $43^{\circ}$  C.

Von Phul testified that Kayser told him in 1907 that he was getting up a patent for a food product and even Burchenal's own testimony shows that Kayser *supposed* that the product he was making was edible. If Kayser at first told him it was not edible he did so when they were negotiating and he wished to keep his process in the dark until he had arranged his terms. That Kayser's statement that it was not edible was not taken seriously by either party is shown by the following testimony:

Q887. But you did not know as a matter of fact whether it would be edible or not? A. I did not. Mr. Kayser stated that it would not be but that was his method of talking.

Both of these men were proceeding soon after Kayser's arrival in this country to develop hydrogenated cottonseed oil as a food product. Even if the thought first occurred to Burchenal I cannot see that he did anything to carry it out in practice. Kayser's patent No. 1,003,035, application for which was filed March 20, 1908, disclosed the process which was employed to make the product covered by the patent in suit, and the specification for this Kayser patent contains the statement that "The time of treatment will vary with the progress realized and with the degree of saturation aimed at." It is to be remembered that Burchenal distinctly disclaimed in his testimony that he had anything to do with the invention of the process covered by the Kayser patents and we thus have a situation where Kayser invented the process and developed the product to the point where it was applicable to use as a food product. He came to America with a sample which as appears from the written record taken from the files of the complainant had a melting point of only  $39^{\circ}$  and developed other samples with melting points of but  $42^{\circ}$  and  $43^{\circ}$  in his March 5, 1908 experiments.

Moreover, it is to be remembered that Crossfield had employed Kayser to experiment in hydrogenating oil, that the former had been in close communication with Normann, who had patented only four years before the process I have mentioned, and that Crossfield had so strenuously objected to the use by Procter & Gamble of the processes of Kayser that they were obliged to purchase their rights to them. It is also noteworthy that Kayser refused to testify in this case and that the witnesses as to the work of Kayser in America are officers or employes of the complainant. Under such circumstances the meagerness of the evidence which has been adduced to show that Burchenal had anything to do with the development of the lard-like food product which is the subject of the patent in suit, coupled with his admission that the entire process under which it was made was the work of Kayser, is most significant and makes it impossible to find that Burchenal invented anything. The defendant has been embarrassed in its defence by many difficulties and has been obliged to go into the enemy's camp to secure almost all its ammunition. In spite of this, it has established that Kayser at the very beginning had developed not only a process but a product little differing from Crisco. Kayser remained with Procter & Gamble until well into 1910, and did not leave America until about July of that year. While there is some general evidence of what Burchenal and others did, or directed, I can find no real proof that anyone but Kayser did anything of substantial moment. No step was taken by Burchenal that could possibly amount to invention.

Complainant urges that the experiments of Kayser and the patents of Normann and Kayser aimed at complete saturation and that neither realized the importance of a partially hydrogenized product. But the process under which their products were made involved in its progress partial hydrogenation, and Kayser's patent No. 1,004,035 distinctly stated that "The time of treatment will vary with the progress realized and with the degree of saturation aimed at." Kayser as far as I can see did everything that was done to develop Crisco, and if his work fell short of this, he achieved enough so that the final step was inevitable to one skilled in the art. Kayser's process was the complainant's process and his product involved a progressive reaction fitted for any purpose. The broad discovery as between him and Burchenal certainly belongs to him.

Furthermore under any fair interpretation of the patent there is no infringement. The file wrapper indicates that the examiner rejected the claims as originally filed saying:

... If the problem of simulating lard from cotton-seed oil were presented to an oil chemist, an incomplete hydrogenization of the cotton-seed oil would at once suggest itself to him as a solution of the problem. All the claims are accordingly rejected on the ... ground of lack of invention.

Thereafter new claims were rejected upon the Kayser patents for the reason *that his process could be arrested at any time to produce an incompletely hydrogenized product*. Then and for the first time Burchenal filed an amendment setting forth certain percentages of linolin, olein and stearin which his product should contain. It seems quite evident therefore that Claims 1 and 2 of his patent would under such circumstances, if valid at all, be limited to substantially the chemical composition described in the amended specification. Indeed the specification closes with the statement that the inventor has produced a product



which "is high in olein, low in linolin and lesser saturated fats and with only enough stearin to make the product congeal at ordinary temperatures."

Under such circumstances it is impossible to treat the melting point as practically the determining factor and if this is not done the defendant's product Kream Krisp does not infringe. After the examiner had held that an incomplete hydrogenation would suggest itself to any chemist seeking to simulate lard and rejected the claims on Kayser, the patentee as I have shown, amended by specifying a particular product and dwelling upon the advantages of a small percentage of linolin to avoid rancidity. If, therefore, the inventor contributed anything to the art it was this special chemical composition which his patent discloses. Claims 1 and 2 should consequently be construed in the light of the proceedings of Burchenal before the Patent Office and not given a scope which would monopolize an art in which Normann, Kayser and others had been the real pioneers.

Kream Krisp has a chemical composition extremely remote from that described in the specification of Burchenal. The following are the relative percentages:

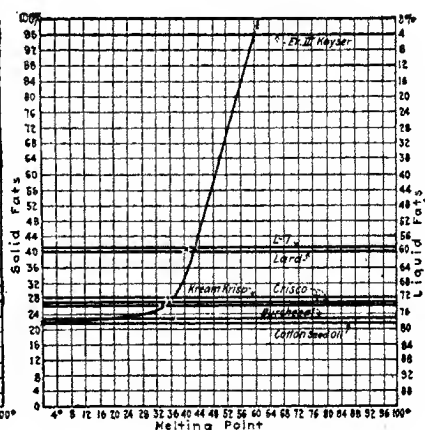
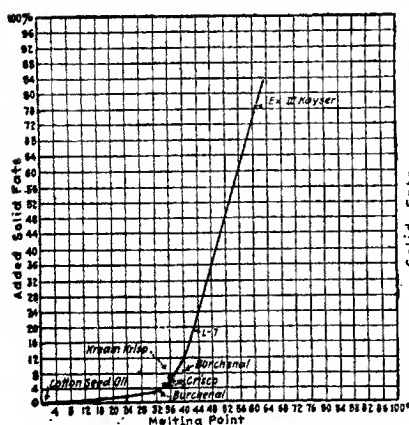
Burchenal.	Kream Krisp.
Per cent saturated fats 20-25	28
Per cent olein 65-75	34.3
Per cent linolin 5-10	37.7

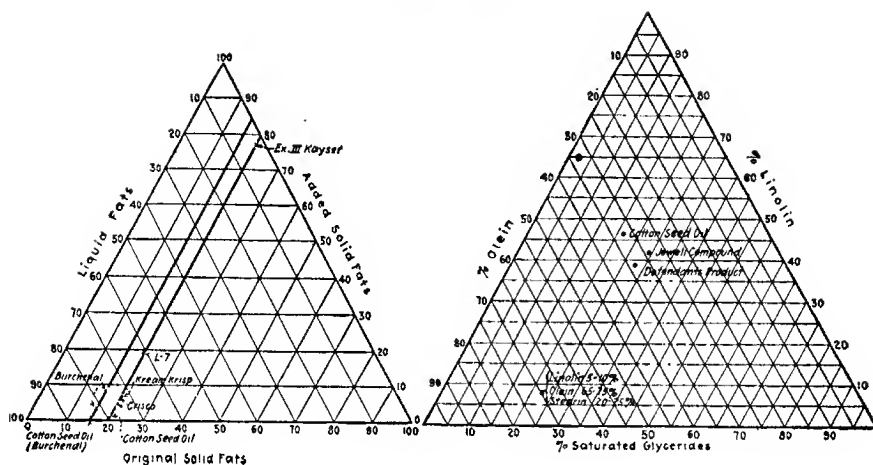
Thus it appears that Kream Krisp instead of being low in linolin is extremely high, and that instead of being high in olein as specified in the Burchenal patent, it has a percentage of olein which differs but little from that existing in refined cottonseed oil unhydrogenated. In fact Kream Krisp seems to present many of the objections referred to in Burchenal's specification and to lack the very things upon which the latter based his right to receive a patent. Indeed the composition is much closer to the lard compound Jewel made out of stearin and cottonseed oil than to Crisco.

The bill should be dismissed with costs because the patent is void for lack of invention and for the further reason that claims 1 and 2 if properly construed are not infringed by the defendant.

Dated, October 3, 1917.

A. N. H., D. J.





In commenting on the decision by Judge Hand in the **Crisco** case, the American Food Journal (October 1917, 567) states:

'This decision has the effect of throwing open to the food industry the right to make a product similar to Crisco, provided that in so doing the manufacturer does not infringe the process patent of E. C. Kayser.

Some few years ago, owing to the rapidly increasing cost of oleostearin, all manufacturers who dealt therein were anxiously casting about for some less expensive substitute therefor. The practice of producing semi-solid compounds made by mixing soft oils with those of stiffer consistency was in vogue in many lines, both industrial and edible, and was recognized as a part of the existent art. The Kayser patent, under which Crisco is made, concerns itself with the method by which hydrogen is made to combine with oleic acid to form stearic acid, the resultant product possessing the characteristics of the saturated fatty acid series—less liability to turn rancid and stiffer consistency.

The Burchenal patent was an attempt on the part of Procter & Gamble to maintain all the rights of a patentee as to the finished product, irrespective of its method of production.

The importance of the suit is readily appreciated when it is realized that should the Burchenal patent have been upheld, it would have tended to stop all inventive work looking toward the production of a product similar to Crisco but made in different fashion. While the courts are generally loath to recognize "product patents" on the ground of their being against public policy, they are, at all times, inclined to maintain the integrity of "process patents," the distinction being very vividly brought out in the present case.

## BURCHENAL PATENT SUSTAINED ON APPEAL

On appeal, the Court found the Burchenal patent was valid and infringed (Judge Hough and Rogers concurring, Judge Ward dissenting). The opinion, written by Judge Hough, reversing the decision of the lower Court states in part,—The patent law does not speak in terms of science, though scientific evidence is necessary for the application of its rules. The chemical composition of steam, water and ice is the same, but they are different things, and in the same commonsense way, oil, lard and stearin are different things, although (with some chemical latitude), the oil may be said ultimately to become stearin, and to pass through the lard stage on the way.

It may be assumed as true that by the mixture of cottonseed oil and animal stearin, a substance can be produced which, for practical purposes, is the same thing as Burchenal's chemically changed cottonseed oil; but one is a mixture and the other is not, and, assuming the difference to be important from the standpoint of either chemist or cook, it is a vital difference from that of the law.

We are, therefore, of opinion that there was invention in Burchenal's disclosure. Product patents may be justly subjected to critical scrutiny, but these claims are far within the border line adverted to in *Fonseca vs. Suarez*, 232 Fed. Rep., 155; and, just as the conversion of an abandoned machine into an operative and successful one by the introduction of new, but simple feature constitutes invention, so we think that seizing upon thing *A*, which has been thing *B*, and was to become thing *C*, and utilizing the half-made but different product amounted to an invention which is duly set forth in this application.

The finding below, that Burchenal was not the inventor of whatever invention is revealed, is really a declaration that one Kayzer did the inventing, and Burchenal, for some inexplicable reason appropriated it. This is an affirmative defence and must be sustained by a fair preponderance of credible evidence. Burchenal swore to invention in the statutory form, and the presumption of validity extends to the identity of the inventor, for certainly nothing could be more completely invalid than a patent for invention to one who invented nothing

\* \* \* \* \*

We are satisfied of the truth (entirely apart from all presumptions) of defendants' testimony that it was not until Kayzer had returned to England, or was on the point of going, that it occurred to anyone that it was not necessary to first harden by hydrogenic saturation the cottonseed oil and then mix it with the fluid article in order to make a lard-like compound—but that the hardening process might be arrested in the manner and for the purposes disclosed by Burchenal's application.

Assuming now that this mental operation or discovery in the sense of the patent law amounted to invention, we not only find no evidence that Burchenal was not the inventor, but it is a strain upon credulity to believe that when this plaintiff corporation might just as well have advanced an application in Kayzer's name it deliberately preferred the fraud of prosecuting it in that of Burchenal.

It may be, and we think is, quite true that the evidence reveals Burchenal as not primarily a chemist, but a man of business deeply interested in the advancement of his corporation's prosperity. We recognize the fact that there is a fundamental difference between "new articles of manufacture and new articles of commerce"; and it may also be quite true that Burchenal's contribution to the sum of human

knowledge grew out of the trained business man's observation of the possibilities of a chemist's process, which he was himself quite incapable of devising.

But just as it is immaterial whether a patentee "understands or correctly states the theory or philosophy of the mechanism which produces" his new result, so it is immaterial whether, when Burchenal observed and seized upon as a new and useful thing a half hydrogenically saturated oil, he was actuated rather by commercial instinct than acquired chemical knowledge. It is enough that he had both a mental conception and a tangible reduction to practice, and that is all that the patent law requires. Quite possibly this patentee would never have conceived the thought, had he not watched Kayzer, but he could and did get something out of Kayzer's train of phenomena, which the latter neither thought of, nor reduced to practice.

The final objection to a decree in plaintiff's favor is that properly construed the claims in suit are not infringed because (a) the defendant's product widely varies from that of the patent in the relative percentages of saturated fats, olein and linolin, (b) the process pursued by defendant in making its product differs radically from that said to be disclosed or assumed in the patent in suit, and (c) that said claims are to be regarded as strictly limited, if not substantially abandoned, through or by reason of the proceedings in the Patent Office as revealed by file wrapper contents.

As to the first point (a) it is enough to note that, while the variation insisted upon is true, it must, to negative infringement, be at least a variation extending beyond the limits of a valid claim read in the light of the disclosure.

In this instance it is not denied that what the defendant makes and sells is not only lard-like, homogeneous in the sense of mixtureless, and wholly consisting of an incompletely hydrogenized cottonseed oil, but it is within the limits of iodine-value, titre and melting points specified in the application. Therefore, it is an infringement.

It is true (b) that defendant's process of manufacture is very different from that of plaintiff, and we are willing to assume it different from and better than anything known to Burchenal or developed by Kayzer. But this patent is upon a product, and, if the product complained of is the patented article substantially as described, it makes no difference by what path or process, new or old, inferior or improved, the infringing product is manufactured.

\* \* \* \* \*

For the reasons stated the decree appealed from is reversed with costs both here and below, and the cause remanded with directions to enter a decree adjudging Claim 1 and 2 valid and infringed.

Judge Ward, in expressing a dissenting opinion, stated that he considered the District Judge right in holding the patent void for lack of invention. To apply semi-solid hydrogenized oil as a substitute for lard in cooking was no doubt novel and useful, but was not, in his opinion, invention. To one skilled in chemical art such use was as obvious as were the many mechanical improvements, which, though new and useful, have been held not inventions within the capacity of those skilled in the art.

There was nothing revolutionary about this new use. Fats satisfactory for culinary needs are abundantly available, yet the complainant is given a monopoly of all semi-solid homogeneous hydrogenized vegetable oils, however produced, when applied to culinary purposes,



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